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Laboratory-Scale Demonstration Using Dilute Ammonia Gas-Induced Alkaline Hydrolysis of Soil Contaminants (Chlorinated Propanes and Explosives)

Victor F. Medina, Scott A. Waisner, Charles Coyle,
Chris Griggs, and Molly Maxwell

June 2016

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Halogenated Propanes," Project number 405711 (PC)

Abstract

Many environmental contaminants are amenable to degradation by alkaline hydrolysis. This project explored the use of ammonia gas to raise soil pH in order to stimulate alkaline hydrolysis. When ammonia gas dissolves in water, it forms ammonium ion, which consumes hydrogen ions (H^+), thereby increasing pH. This study established that 5% ammonia in air can increase soil pH from 7.5 to 10.3. Batch studies indicate that this pH increase can stimulate alkaline hydrolysis reactions, resulting in the degradation of chlorinated propanes (trichloropropane, dichloropropane) and explosives (2,4,6-trinitrotoluene, nitrobenzene, and RDX). A column study was conducted focusing on evaluating the penetration of ammonia and subsequent pH change. The study showed pH penetration of 20 cm in a 2.5 cm diameter column over 7 days, with a flow of 5% ammonia gas at 1 sccm. Chlorinated propane concentrations were reduced from levels of as high as 2400 ug/kg to as low as non-detect. A small amount of these were captured in the column off gas. The team also explored whether ammonia gas exposure could stimulate metabolic activity of ammonia-oxidizing microorganisms. A 283-day experiment did not result in any measureable increase in ammonia-oxidizing microorganisms, but the team found significant increases in soil nitrogen concentrations.

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Preface

The work reported herein was conducted at the U.S. Army Engineer Research and Development Center (ERDC), Environmental Laboratory (EL), Vicksburg, MS and at the U.S. Army Corps of Engineers (USACE) Huntsville District. The project was funded primarily by the Strategic Environmental Research and Development Program / Environmental Security Technology Certification Program (SERDP/ESTCP) and United States Environmental Protection Agency (USEPA). Support from USEPA included laboratory analysis of samples via Region 9 Laboratory, in addition to funding from headquarters, USEPA (HQEPA). A small amount of funding from the Formerly Used Defense Sites (FUDS) program was used to test the applicability of the process to explosives-contaminated soil.

The authors would like to acknowledge Dr. Andrea Leeson (SERDP/ESTCP), Greg Gervais (HQEPA), and John Quander (HQEPA, retired); all three were instrumental to initiating this project. Critical support was also received from Bruni Davila (EPA, Region 9), and Richard Bauer (EPA, Region 9 Laboratory). Peer review was provided by Dr. Heather Knotek-Smith and by Deborah Felt of ERDC-EL.

At the time of publication of this report, Dr. W. Andy Martin was Chief of the Environmental Engineering Branch; Warren P. Lorentz was Chief of the Environmental Processes and Engineering Division; Dr. Elizabeth Fleming was the Director of EL; COL Bryan S. Green was Commander of ERDC; and Dr. Jeffery P. Holland was ERDC Director.

Acronyms

ABC	Ammonia Buffering Capacity
AFB	Air Force Base
AMO	Ammonia Monooxygenase
bgs	below ground surface
CCL	Contaminant Candidate List
cm	centimeter(s)
DBCP	1,2-dibromo-3-chloropropane
DCE	Dichloroethene
DCP	Dichloropropane (1,2- and 1,3- isomers)
DNT	Dinitrotoluene (2,4- and 2,6- isomers)
DoD	Department of Defense
EL	Environmental Laboratory
ERDC	Army Engineer Research and Development Center
EP, EPE	Environmental Processes Division, Environmental Engineering Branch
ESTCP	Environmental Security Technology Certification Program
FUDS	Formerly Used Defense Sites
FY	Federal Fiscal Year (Typically from 01 October to 30 September)
g, Kg, mg, µg, ng	gram, kilogram, milligram, microgram, nanogram
gal	gallon(s)
GEDIT	gaseous electron donor injection technology
in.	inch

L, mL	liter(s), milliliter(s)
LBC	Lime Buffering Capacity
m, mm, cm	meter(s), millimeter(s), centimeter(s)
MCL	Maximum Contaminant Level
mgd	million(s) gallons per day
MTBE	Methyl-tert-butyl-ether
NB	Nitrobenzene
PBOW	the former Plum Brook Ordnance Works
QAPP	Quality Assurance Project Plan
qPCR	quantitative Polymerase Chain Reaction
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
SAD	Sioux Army Depot
scc	standard cubic centimeter(s)
sccm	standard cubic centimeter(s) per minute
sec	second
SERDP	Strategic Environmental Research and Development Program
TCE	Trichloroethene
TCP	1,2,3-Trichloropropane
TKN	Total Kjeldahl Nitrogen
TNT	2,4,6-Trinitrotoluene
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
rpm	revolutions per minute
USACE	United States Army Corps of Engineers
USAF	United States Air Force

USDoD	United States Department of Defense
USEPA	United States Environmental Protection Agency
VOA	Volatile Organic Analysis vial.

1 Introduction

Study objective

The goal of this research effort was to perform bench-scale studies that would serve as a proof-of-concept for development of a novel process for in situ treatment of contaminants susceptible to alkaline hydrolysis that are present in vadose-zone source areas. The process could also be used to cut off leaching of contaminants from surficial and vadose-zone source areas, preventing continued mass transfer to groundwater. The treatment process is initiated via the injection of ammonia gas, which increases soil pH when the gas dissolves in moisture found in the soil.

Background

Vadose remediation

Although remediation technology development has been focused mostly on groundwater treatment in recent years, the importance of vadose zone contamination has been gaining attention (Newell et al. 2013, Wellman et al. 2012) as well. Characterization of the vadose zone has often been overlooked during remedial investigations. However, vadose zone source areas are commonly found when detailed investigations are undertaken. A long-term trend of aquifer drawdown has also been recognized in parts of the United States (McGuire 2009), especially in areas where groundwater is relied upon for irrigation and drinking water. If groundwater levels continue to recede, it is expected that new vadose-zone source areas will emerge; i.e., shallow, saturated-zone source areas may become vadose-zone source areas as the level of the water table recedes. Groundwater can be very challenging to treat. For example, a relatively small aquifer with 2,4,6-trinitrotoluene and RDX contaminants at the Umatilla Army Depot was treated by pump and treat for nearly 20 years (1994 to 2012), and following that, efforts were made to treat the residual explosives, which still exceeded treatment goals, by biological degradation (Medina et al. 2012, Michalsen et al. 2013). Gases are easier to distribute in soils than liquid amendments are in groundwater aquifers. Directly attacking vadose-zone source areas and cutting off leaching pathways may be a more cost-effective course of action than allowing contaminants to leach into groundwater before initiating treatment.

Gas phase remediation

Gas phase remediation has been studied for a range of contaminants. Soil vapor extraction (USACE 2002), steam injection (Davis 1998, Peng et al. 2013), and air sparging (Johnson et al. 1991) are commonly used remediation technologies to remove volatile contaminants from soil and groundwater, respectively. Similarly, bioventing (USACE 2002) and biosparging are means to use gas to stimulate bioremediation in soil and groundwater by adding oxygen. These methods are very well established and are commonly applied as presumptive remedies (USEPA 1997), so the authors will not cover these further in this document.

This study focuses on the use of gases as a means for degrading or transforming contaminants. This approach has been studied less than other processes have, but there are compelling examples of effectiveness in the literature. There are two general methods. In the first method, gases can be used to manipulate master variables, particularly pH and/or redox potential (Denham and Looney 2007). Hydrogen sulfide gas, for example, has been used to reduce metals in soils, resulting in stabilization of metals (like Cr (VI)) and radionuclides (uranium or technetium) (Thornton and Amonette 1999, Thornton et al. 2007). Master variable manipulation is generally reversible (the pH or redox potential will return back to original levels), but this is not a problem as the process results in contaminant degradation. However, if the reversal reaction is slow, the process could still be an effective management approach for metals stabilization.

In the second method, a chemical reaction is created, resulting in degradation or transformation of the target contaminant. Gaseous phosphate has been studied to create stable metal/radionuclide complexes that are irreversible (Denham and Looney 2007). Ozone, for example, has been studied for injection into the subsurface to directly oxidize organic contaminants (Choi et al. 2002). It is effective, but will eventually dissipate.

Gases can also be injected to stimulate desirable biological activity. Methane has been studied as a gaseous supplement to stimulate cometabolism of chlorinated solvents, such as trichloroethene (TCE) and applied full-scale at the Savannah River site in Aiken, SC (Pfiffner et al. 1997). Similarly, propane has been injected to stimulate co-metabolism of chlorinated solvents (Dacyk and Hughes 1999) and methyl-tert-butyl-ether (MTBE); hydrogen and propane gases were used to stimulate

biodegradation of chlorinated solvents like TCE and dichloroethene (DCE) (Newell et al. 2013). Rainwater et al. (2002) documented a field study to treat explosives (TNT and RDX); the study involved creating reducing conditions by flooding the soil with nitrogen gas. Evans (2010) treated perchlorate in vadose zone soils by the injection of an unspecified gaseous electron donor (gaseous electron donor injection technology or GEDIT).

Ammonia has been studied for its ability to increase pH (Zhong et al. 2015). Ammonia gas diffusion is primarily a factor of water content in the soil, and partitioning into pore water is relatively fast, creating pH increases up to 13.2. The process was very effective for the stabilization of uranium (Szecsody et al. 2010, Szecsody et al. 2011, Zhong et al. 2015) and technetium (with supplemental hydrogen sulfide gas, Szecsody et al. 2015). The pH change is reversible, but the change is slow enough to make the process a potentially effective management approach.

Importance of water content

There is strong evidence that effectiveness of vadose-zone treatment processes is dependent on moisture content. Bioventing is one of the most extensively studied vadose treatment processes, and there are studies indicating that degradation rates will be limited if conditions are too dry. A column study using soils from a site in Utah exhibited higher fuel biodegradation rates as the soil moisture content was increased from 6 to 18 % (Hinchee and Arthur 1990). In addition, Bezerra and Zytner (2003) reported that optimum soil water content for bioventing is 18% by weight, or approximately 50% of soil field capacity (Bezerra and Zytner 2003).

At a site in southern California (Twentynine Palms Marine Corps Base) with very low initial moisture content (2-4% by weight), it was shown that substantial increases in degradation rates could be achieved through addition of moisture (Zwick et al. 1995; Zwick et al. 1997). Biodegradation rates were increased from 0.1 to 1.5 mg/kg/day at a depth of 10 ft, based on in situ respiration testing. A drip irrigation system, with the rows of drip-lines placed about 2 ft below ground surface (bgs), was used to increase moisture content at the Twentynine Palms site; and a down-hole neutron probe was used to measure moisture content. Following irrigation, a substantial increase in moisture content was observed down to a depth of approximately 10.7 m (35 ft). Below 12.2 m (40 ft), there did not appear to be a significant increase in moisture content. The moisture-penetration depth at the Twentynine Palms site was aided by the relatively

uniform, sandy soils (only slightly silty), and the unusually homogeneous soil profile. Low permeability lenses, and other types of complex features that are commonly present in the subsurface at many sites, would reduce the effectiveness of a shallow, near-surface irrigation system.

Bioventing is different than the reactive gas process because bioventing is a microbially mediated treatment process, whereas the reactive gas process is primarily a chemical treatment process. However, for both processes, the degradation reactions occur predominantly within the aqueous phase, or at the interface with the aqueous phase; and the reactions are unlikely to proceed until after the contaminants (and reactants) have dissolved into the pore water or soil moisture.

As the moisture content increases beyond a point, penetration of the reactive gas mixture into the soil matrix will be impeded due to blockage of pore spaces by moisture. To maximize penetration of the reactive gas mixture throughout the soil matrix within the treatment zone, a case can be made for initially avoiding any attempts to increase moisture content. If moisture addition is determined to be necessary, it should usually be delayed until after an initial period of reactive gas injection. After full penetration of treatment zone by reactive gas has been shown to have been achieved, then a subsequent round of injection of humidified air may be warranted. Injection of humidified air would then be followed by another round of reactive gas injection.

During full-scale bioventing at Kirtland Air Force Base (AFB), humidified air was injected during a bioventing project in an area with dry soils (USAF 1999). The humidified air was injected by routing the air from the blower through a partially filled drum of water before distributing the air to the injection wells. The relative humidity of the air was increased to the range of 80 to 100%, by bubbling the air through water prior to injection, using a porous stone to create fine bubbles.

The humidified air was injected for a period of about two months. The total volume of water moved into the soil during the two-month period was estimated to be 366 gal. However, there appeared to be a problem with use of a long-screened injection well, causing preferential flow into deeper zones, below the primary area of interest. Measurable increases in soil moisture content, within the primary zone of interest, were not observed; this was probably due to the limited number of soil samples

collected, soil heterogeneity, and preferential air flow into specific depth intervals. It was thought that most of the humidified air moved into deeper zones, below the primary treatment zone. However, significant increases in microbial populations were observed in some monitoring points, and it was concluded that the use of humidified air did prevent further drying of the already dry soils from occurring.

Approach

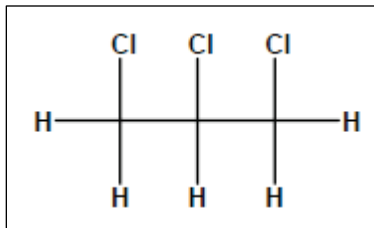
Alkaline hydrolysis

Alkaline hydrolysis describes an abiotic nucleophilic reaction in which the attacking nucleophile is a hydroxide ion resulting from the dissociation of water. These conditions occur when the pH is basic or alkaline. Nucleophilic reactions are particularly effective for esters and amides. There are several key contaminants that are amenable to alkaline hydrolysis; these contaminants are discussed below.

Halogenated Propanes

Halogenated Propanes, particularly 1,2,3-trichloropropane (TCP, see Figure 1 for structure), have been identified as emerging contaminants by both the USEPA (Cooke 2008) and the U.S. Department of Defense (USDOD). TCP is a known carcinogen, and although a maximum contaminant level (MCL) has not been set by the USEPA, in 2009, the California Department of Public Health set a State Notification Level of 0.005 mg/L and Public Health Goal of 0.0007 mg/L for TCP in drinking water (see <http://oehha.ca.gov/water/phg/123tcp082009.html>). TCP is found in the latest version of the drinking water contaminant candidate list (CCL) proposed by EPA (USEPA 2008).

Figure 1. Structure of 1,2,3-trichloropropane.



TCP can be manufactured alone, but it is also found in many chemical formulations as an intermediary by-product (Kielhorn et al. 2003). It is a

component in soil fumigants for the control of pests and nematodes (Kielhorn et al. 2003). In addition, TCP was in solvent mixtures and a component in tank sealants. It has been found in groundwater in at least 45 Department of Defense (DoD) installations and in soil in 27 of these installations (Hunter et al. 2006). Sites contaminated with TCP typically have other halogenated propanes, including 1,2-dichloropropane (DCP), 1,3-DCP, and 1,2-dibromo-3-chloropropane (DBCP). Because of its use as a solvent, it is also frequently found with chlorinated solvents like trichloroethene (TCE) and carbon tetrachloride.

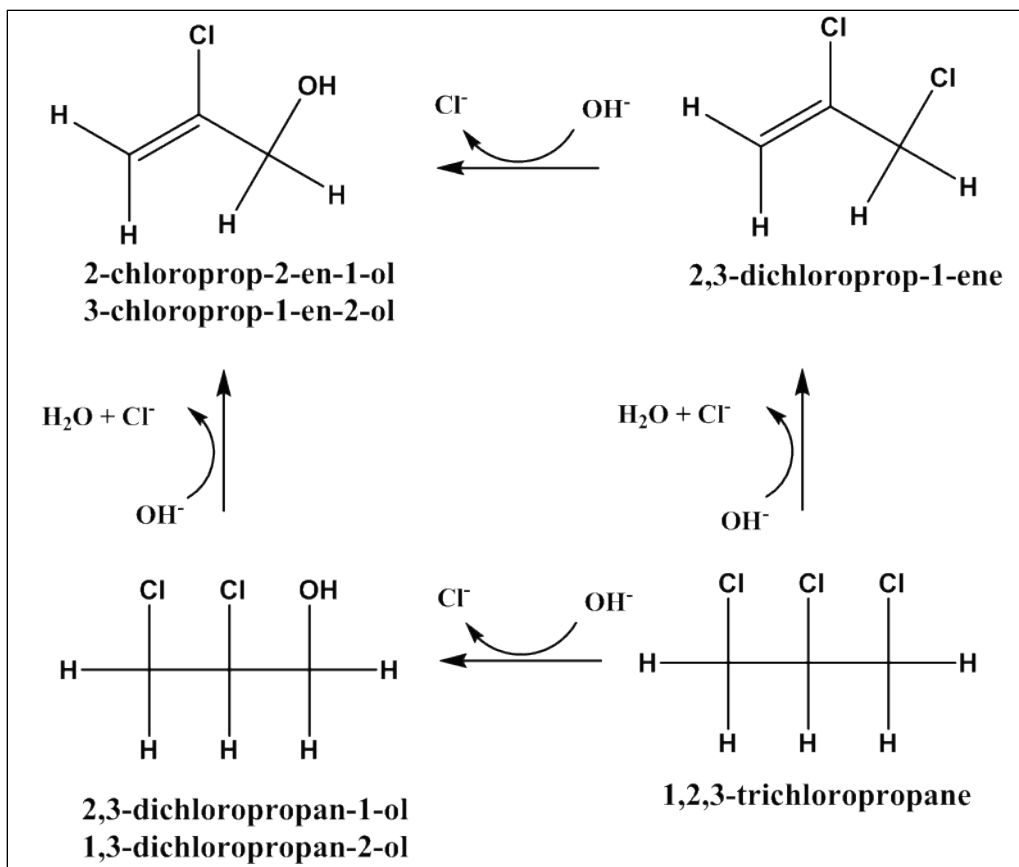
TCP is not as volatile as compounds like TCE (vapor pressure of TCP = 3.1 mm Hg vs. TCE 131.5 mm Hg, see Table 1, Tratnyek et al. 2008); therefore, it is not particularly amenable to treatments like soil vapor extraction. It is resistant to biodegradation as well as to most forms of abiotic treatment (Tratnyek et al. 2008). Reduction with palladized iron has shown some efficacy of promoting reductive degradation (Tratnyek et al. 2008).

Table 1. Boiling points and vapor pressures of compounds used in our halogenated propane studies. (Source: NIOSH 2007).

Compound	Boiling Point (C)	Vapor Pressure (mm Hg)
Chloroform	61.15	25.9 @25C
1,2-dichloropropane	95-96	40 @19.4C
1,3-dichloropropane	120-122	15.0 @20C
1,2,3-trichloropropane	157	3.1 @25C
1,2-dibromo-3-chloropropane	196	0.8 @21C

Alkaline hydrolysis of TCP has been studied in aqueous systems. Rates published by Pagan et al. (1998) suggest potential for effective remediation. Based on the Arrhenius constant ($\log A = 13.31 \pm 0.53$), the team estimated that effective treatment could be achieved at elevated temperatures on the order of 60 °C at modestly elevated pHs in the 8 to 9 range. However, the team hypothesized that higher pH may allow for effective treatment without the need for temperature elevation. Free energy calculation from ab initio (ab initio are computational methods based on the most fundamental thermodynamic properties of the molecules of interest) electronic structures indicate that OH⁻ nucleophilic substitution is thermodynamically favorable ($\Delta G^\circ \sim -25\text{kcal/mol}$) (Bylaska et al. 2010). Figure 2 is a proposed pathway for TCP degradation via alkaline hydrolysis, based on Bylaska et al. (2010).

Figure 2. Pathway for TCP degradation by alkaline hydrolysis (OH^- nucleophilic substitution) as proposed by Bylaska et al. (2010).



In addition to TCP, this team investigated several other compounds in the study:

- Chloroform
- TCP
- 1,2-dichloropropane (1,2-DCP)
- 1,3-DCP
- 1,2-dibromo-3-chloropropane (1,2-DB-3-CP)

1,2-DCP, 1,3-DCP are potential breakdown products of TCP. 1,2-DB-3-CP is a potential co-contaminant with TCP. Chloroform is a chlorinated methane that could be amenable to alkaline hydrolysis. Although TCP has a relatively low volatility, some of these other compounds are, in fact, quite volatile (Table 1).

Explosives

Explosives are the most widely studied compounds for degradation by alkaline hydrolysis as a soil/groundwater remediation approach. Research has particularly focused on 2,4,6-trinitrotoluene (TNT), dinitrotoluenes (DNT, 2,4- and 2,6-), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) (Larson et al. 2012). Although any caustic additive can potentially be used to stimulate these reactions, the majority of applications have either used hydrated lime or sodium hydroxide mixed in the soil or water. Larson et al. (2012) contains a relatively recent review of the treatment of explosives by alkaline hydroxide.

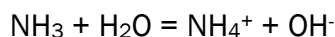
Other contaminants

Alkaline hydrolysis can transform and degrade a wide range of chemicals. However, only a few of these are environmentally significant. Some environmentally significant contaminants that have shown potential for treatment by alkaline hydrolysis include:

- various chlorinated compounds (Pagan et al. 1998);
- certain pesticides, like atrazine and parathion (Howard 1991) and 2,4-D (Zepp et al. 1975); and
- polychlorinated biphenyls (PCBs) (Medina et al. 2007, Waisner et al. 2008, Waisner et al. 2011).

Ammonia and Soil pH

Air phase ammonia can dissolve in water to form ammonium, thereby increasing pH:



The portioning in water is predictable, following Henry's Law (Hedengren et al. 2000). In soils, this reaction will occur in the soil moisture regime and is well established to increase soil pH. This reaction is recognized to increase soil pH in agricultural soils when fertilizers like anhydrous ammonia are applied (Kyveryga et al. 2004).

Szecsody et al. (2011) explored pH elevation from ammonia injection as a means for stabilizing uranium in soil. Relatively dilute ammonia-in-air mixtures elevated soil pH to levels ranging from 11 to 13. These levels were

successful at significantly reducing uranium mobility, although the effect was somewhat reversible.

Ammonia oxidation and remediation

Ammonia oxidizing microorganisms are chemo-autotrophic microorganisms; most are of the genera *Nitrosomonas* and use the oxidation of ammonia to create energy to convert carbon dioxide to organic matter. The aerobic reaction is catalyzed by the enzyme ammonia monooxygenase (AMO). Ammonia monooxygenase is interesting because it has been found to co-metabolize recalcitrant chlorinated solvents, like carbon tetrachloride and trichloroethene (TCE) (Rasche et al. 1991, Vannelli et al. 1990). Because the pH-increasing reaction also adds ammonia into the soil moisture environment, the same process may be used to stimulate AMO activity, and co-metabolic degradation of a number of chlorinated solvents.

2 Materials/Methods

Experiments

Consistent with projects funded by the USEPA, a Quality Assurance Project Plan (QAPP) was prepared for the portions of work funded by the USEPA. The QAPP was titled “Reactive Gas Study to Promote Alkaline Hydrolysis of Halogenated Propanes.” The QAPP was authored by Dr. Victor Medina, with input by Scott Waisner and Chuck Coyle. In the interest of brevity, the QAPP is not appended to this report, but can be obtained from the authors. Experimental plans are included in Appendix 1. Any deviations or modifications from the QAPP are provided in this write up.

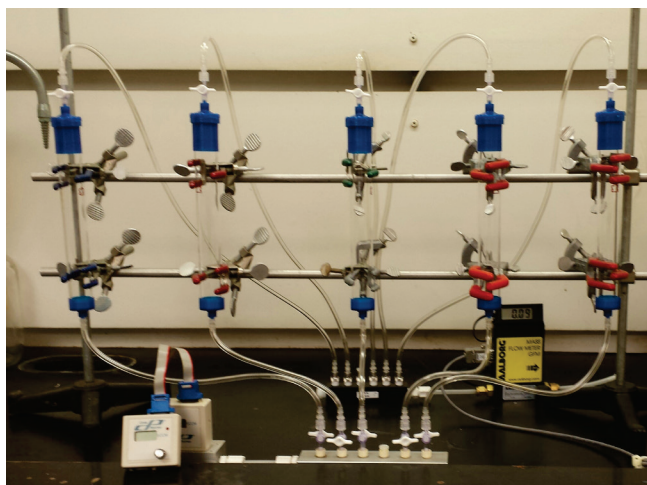
Evaluation of pH increase via Ammonia Gas

The purpose of this experiment was to evaluate the efficacy of using ammonia gas to elevate soil pH. A column experiment was designed and executed to achieve this goal.

Experimental Apparatus

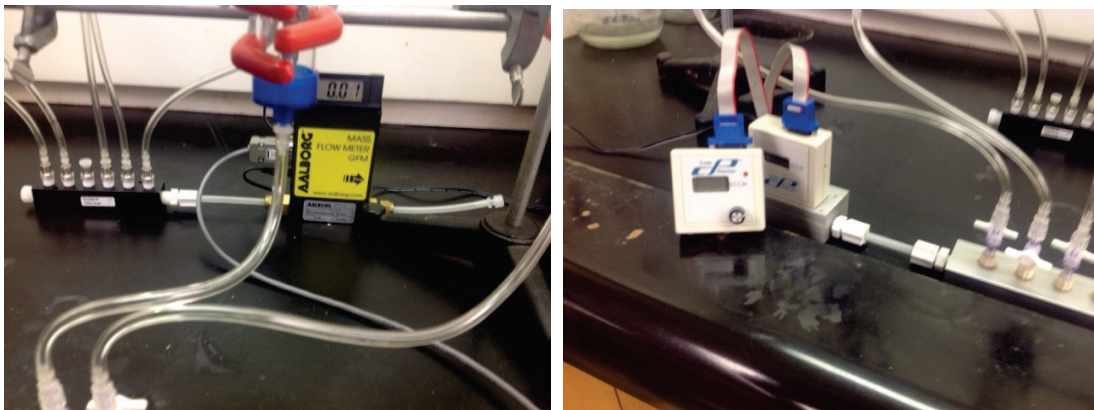
A simple column apparatus was prepared, consisting of 2.5 centimeters (cm) diameter x 20 cm long (1 in. diameter x 8 in. long) glass columns (Figure 3) with air-tight, Luer-lock fittings (Sigma-Adrich, C4794).

Figure 3. Column apparatus for pH elevation study.



Gas flow into the column was regulated by a gas mass flow controller and confirmed on the outlet by a gas mass flow meter and totalizer (Figure 4).

Figure 4. Flow meter (right) and flow totalizer used in the column studies.



Gas was provided by a custom-made mixture, prepared by Airgas, Inc. (Figure 5). The pressurized control made it possible to precisely control the gas flow and pressure.

Figure 5. Custom 5% ammonia gas cylinder prepared for the project.



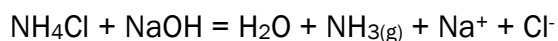
Experiments

Columns were treated with a constant flow (1 standard cubic centimeter per minute [sccm]) of the 5% ammonia at specific times to meet target total gas volumes (15, 25, 75, 250, and 1150 standard cubic centimeters [scc]). After the desired treatment time, the columns were disassembled and the soil was carefully removed into two batches, the bottom (influent) and top (effluent). Each soil batch was analyzed for pH (see below).

Treatment of halogenated propanes by ammonia-gas-induced alkaline hydroxide

Initial screening with soils spiked with the target halogenated propanes indicated that volatile losses would likely be substantial, making it difficult to determine the effectiveness of the hydrolysis reaction. Therefore, the efficacy of treatment by batch reactors was evaluated. Two mechanisms were explored to treat the soil; the first was the use of 7 N ammonia in methanol (Sigma Aldrich). The 7 N ammonia could be placed in an open tube and allowed to evaporate — this method was found to increase the soil pH from an initial value of 7.8 to approximately 8.8. Unfortunately, this upper level was not sufficient to reach the estimated necessary pH levels to affect the alkaline hydrolysis reaction.

A second method was developed and screened, involving the reaction of NH_4Cl and NaOH , as follows:



The reaction proved to be effective at increasing soil pH to levels greater than 10 (Table 2), the level sufficient to meet the conditions estimated to stimulate alkaline hydrolysis reactions for halogenated propanes.

Although the reaction between NH_4Cl and NaOH was exothermic, the soil was never in direct contact with the above reagents. The outside of the jars did not become warm to the touch during the reaction; however, the team did not directly measure the temperature. If any temperature increase occurred, it is believed to have been very slight.

The reactant-containing vial was enclosed within an outer jar, with the soil in the bottom of the jar. If a slight increase in temperature did occur, it would have returned to background temperature relatively quickly, and the experiments were of sufficient length to allow ample time for the ammonia to react with the soil in the bottom of the jar (at least nine days, see below).

Table 2. Scoping experiments with $\text{NH}_4\text{Cl}/\text{NaOH}$ reaction.

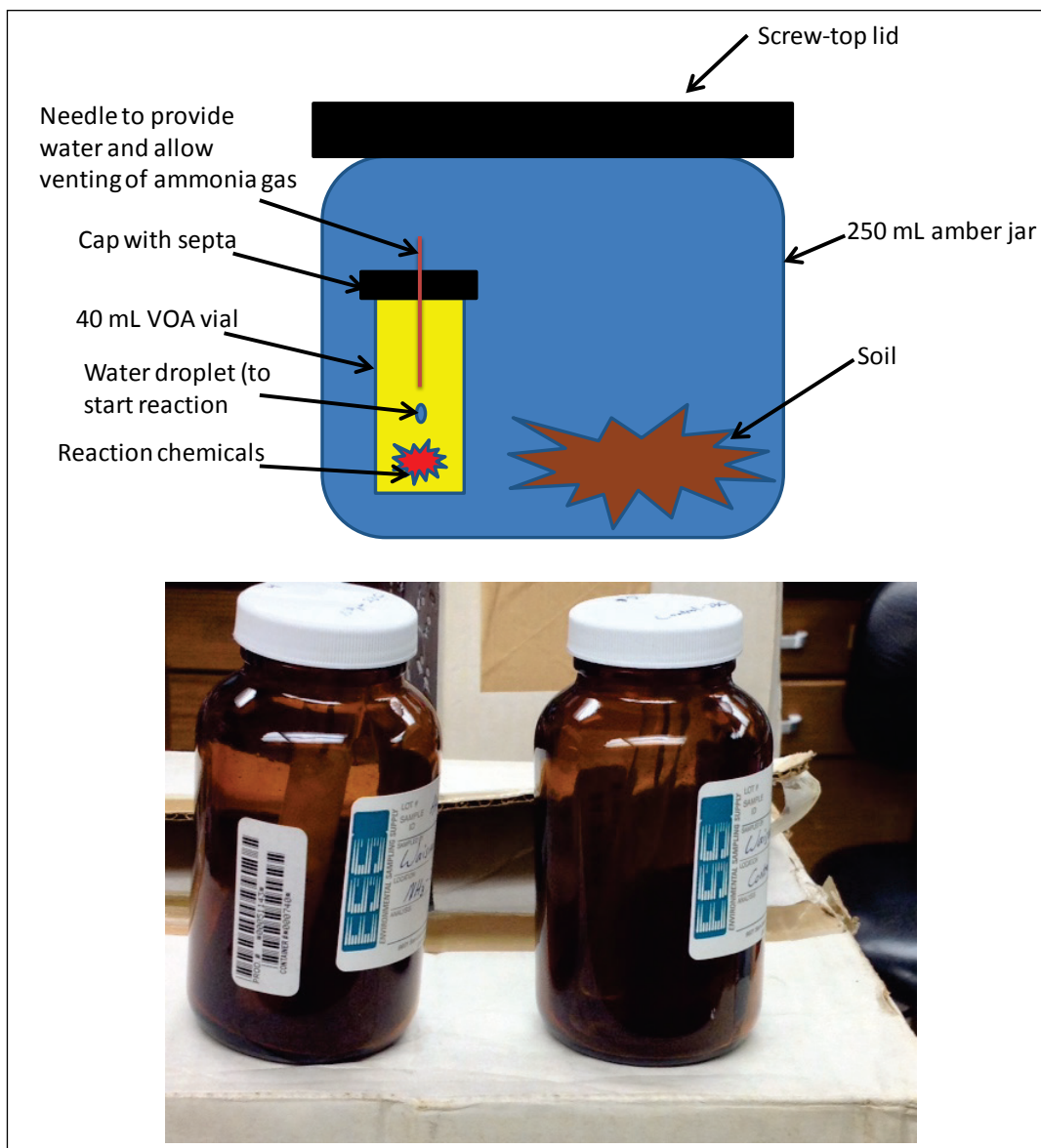
NH_4Cl (g)	NaOH (g)	H_2O (mL)	Soil (g)	Reaction time (days)	pH
5.03	5.01	0	64.75	6	10.8
1.57	1.18	20	100.20	8 16	10.09 10.14
0.79	0.59	20	102.14	8 12	9.78 9.79
0.39	0.31	20	100.20	1 2 8	9.32 9.59 10.17
0.196	0.148	20	100.10	1 7	9.15 9.81

The soils were spiked with a mixture of the following constituents:

- Chloroform
- TCP
- 1,2-DCP
- 1,3-DCP
- DBCP

An experimental approach was developed, as shown in Figure 6. Two hundred fifty mL screw-top amber jars were used as batch reactors. Spiked soil (see materials/methods section for source of soils) was added to each reactor and sealed. A 40 mL volatile organic analysis (VOA) vial was prepared with about 6.7 g NH_4Cl and 5.0 g NaOH . A needle was used to puncture the septa on the VOA vial and a drop of water was placed in to start the chemical reaction forming ammonia. The reactor was opened, the VOA vial was placed in, then the reactor was sealed again. The ammonia could migrate out of the VOA vial through the needle. For Test 1, the reactors were incubated for 14 days (336 hours). The incubation time for Test 2 was 9 days (216 hours). Both tests were conducted at two temperatures, 23° and 62°C. The results of the treatments were statistically compared to the controls using paired student t-tests, $\alpha < 0.001$.

Figure 6. Schematic (top) and picture (bottom) of batch reactors used for halogenated propane and explosives degradation studies. The tube used for the ammonia-producing reaction is visible in the two reactors.



As discussed in the results, two experiments were run, Test 1 and Test 2. The procedures were similar for both experiments, but there were some differences. The soil mass in Test 1 was 100 g and 70 g in Test 2. Spiking the soils proved challenging, presumably due to the volatility of the organic species. The mass of contaminant added to the soil included the total mass required to saturate the headspace of the container and the mass of contaminant desired in the soil. **Error! Reference source not found.** summarizes the spiking of the two soils. To spike soils, soil was added to a 6 L ceramic mixing drum. The liquid contaminant was withdrawn from the source vial and sprayed onto the soil via a syringe.

The mixing drum was sealed and placed on a drum roller for a minimum of three days. The soil was taken directly from the drum, weighed, and placed into the test jars. Prior to Test 2, three samples were also collected directly from the drum for contaminant analysis.

Table 3. Spiking for halogenated propane degradation experiments.

Contaminant	Source Conc. (Sigma-Aldrich)	Volume (ml)
Chloroform*	99%	6.20
1,2,3-TCP	99% (110124)	0.150
1,2-DCP	99% (D72182)	1.50
1,3-DCP	99% (D72204)	0.670
1,2-DB-3-CP	97% (676713)	0.075

* Not included in test 2

Treatment of explosives by ammonia-gas-induced alkaline hydroxide

An exploratory study on the efficacy of treating explosives with ammonia gas to stimulate alkaline hydrolysis was conducted. The study used the same experimental procedure discussed above for the treatment of halogenated propanes. The 14-day study focused on the treatment of 100 g of explosives-contaminated soils (see materials below).

Penetration of pH increasing reactions in a column study

A column study was prepared to study the penetration of ammonia and its effect in elevating pH over a more extended period of time (seven days). The study was conducted as a series of glass column segments connected together in sequence. Although the main focus was on pH penetration, the soils were also spiked with halogenated propanes, so the team could study their fate.

Column setup

A test column was prepared consisting of 10 glass segments that were linked together with segments of Tygon tubing. Each segment was 20 cm long x 2.5 cm diameter (8 in. long x 1 in. diameter, Figure 7).

Figure 7. Set up for column study. Columns were set up to flow in series.



Soil

Approximately 1.5 L of soil was measured (about 0.9 L was required to fill all the columns). The background moisture content of the soil was measured to be approximately 7%; the pH was 7.5, and the soil was sieved through a No. 18 (1.00 mm sieve). Water was added to the soil to reach about 12.4%, which was determined to be sufficient for the experiment. The soil was spiked with a mixture of 1,2-DCP, 1,3-DCP, TCP, and DBCP; the mixture is described in Table. The spiking targeted approximately the same levels of the halogenated propanes — which had elevated DCP levels — used in the batch tests. A minimum of 72 hours of mixing in a ceramic ball mill tumbler was used to homogenize the soils — a method that was very effective in the team's previous experiments (it is necessary to mix after spiking to uniformly distribute the contaminants). Nine segments were filled with the spiked soil. The last segment, segment 10, was filled with unamended soil to serve as an initial trap for moisture and contaminants. One sample was collected for analyses from the mixing drum prior to packing each column to provide an initial starting condition for the test column.

Table 4. Spiking for halogenated propane column experiments.

Contaminant	Source Conc. (Sigma-Aldrich)	Volume (ml)
1,2,3-TCP	99% (110124)	0.170
1,2-DCP	99% (D72182)	1.60
1,3-DCP	99% (D72204)	0.700
1,2-DB-3-CP	97% (676713)	0.100

Treatment by ammonia gas

The columns were treated with 5% ammonia gas at a flow rate of 1 sccm. To quantify penetration, it was best if ammonia saturation did not exceed the total column length. At this rate, based on the background work, it was estimated to take about 10 days to saturate 5 columns. Therefore, a seven-day saturation period was selected, which the team estimated would complete saturation of 3 columns and partial saturation of a fourth column. The saturation period was selected to allow observations of tailing effects as well as to provide a sufficient margin of safety.

Column takedown and sampling

After gas exposure, the columns were taken apart. The soil from each column was carefully removed and divided into two segments (inlet and effluent portions); each segment consisting of about 60 g (the team's analyses required a total of 45 g per segment). The soil was tested by the analytical regiment described below, allowing for the graphical representation of 20 data points versus distance.

Analyses

Soils were analyzed for pH, ammonia, nitrate, and nitrite – all of which were performed at ERDC. Total Kjeldahl Nitrogen was analyzed by a contract laboratory. 1,2-DCP, 1,3-DCP, TCP, and 1,2-DB-3-CP in soil were analyzed by EPA Region 9's analytical laboratory.

Effluent trap

Sorbent tubes were obtained from SKC Inc., Chromosorb 102, and used as effluent traps to trap any contaminants stripped from the columns (Figure 8).

Figure 8. Sorbent tubes used as after-column traps in column experiment.



Tubes were sampled and initially stored in a 4 °C freezer. After the decision was made to analyze the sorbent tubes, they were shipped (preserved with ice) with a chain of custody (Figure 9).

Sorbent tubes were extracted and analyzed by Beacon Environmental Services (Forrest Hills, MD), who reported the results as ng of contaminant trapped by the tubes.

Figure 9. Sorbent tubes packaged for shipping and chain of custody.

Form to be completed and returned to PAFY Tunnings, Bldg. 3299, Rm. 113, Est. 4826

Analysis will not begin until this form is received. *A valid D-10 is required in advance.*

Person submitting samples: Scott Wainner
 P.I. name: Scott Wainner
 Project Name: Ammonia gas
 Extension to be reached at: 2286
 #3058

People to receive report: ☒ P.I. ☐ Submitter ☐ Other:
 Special considerations (High concentrations, non-standard matrix, e.g.):

#	Sample ID	Sample Date	Sample Matrix	Preservative	Analysis Requested
1	C1 E10	6/1/15	Sorbent tube	AC	TD-17
2	C2 E10	6/1/15	Sorbent tube	AC	TD-17
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					

To be completed by ECR: *Free free to attach any additional instructions*
 Date Received: 6/1/15 Receiving Person: Scott Wainner Page 1 of 1

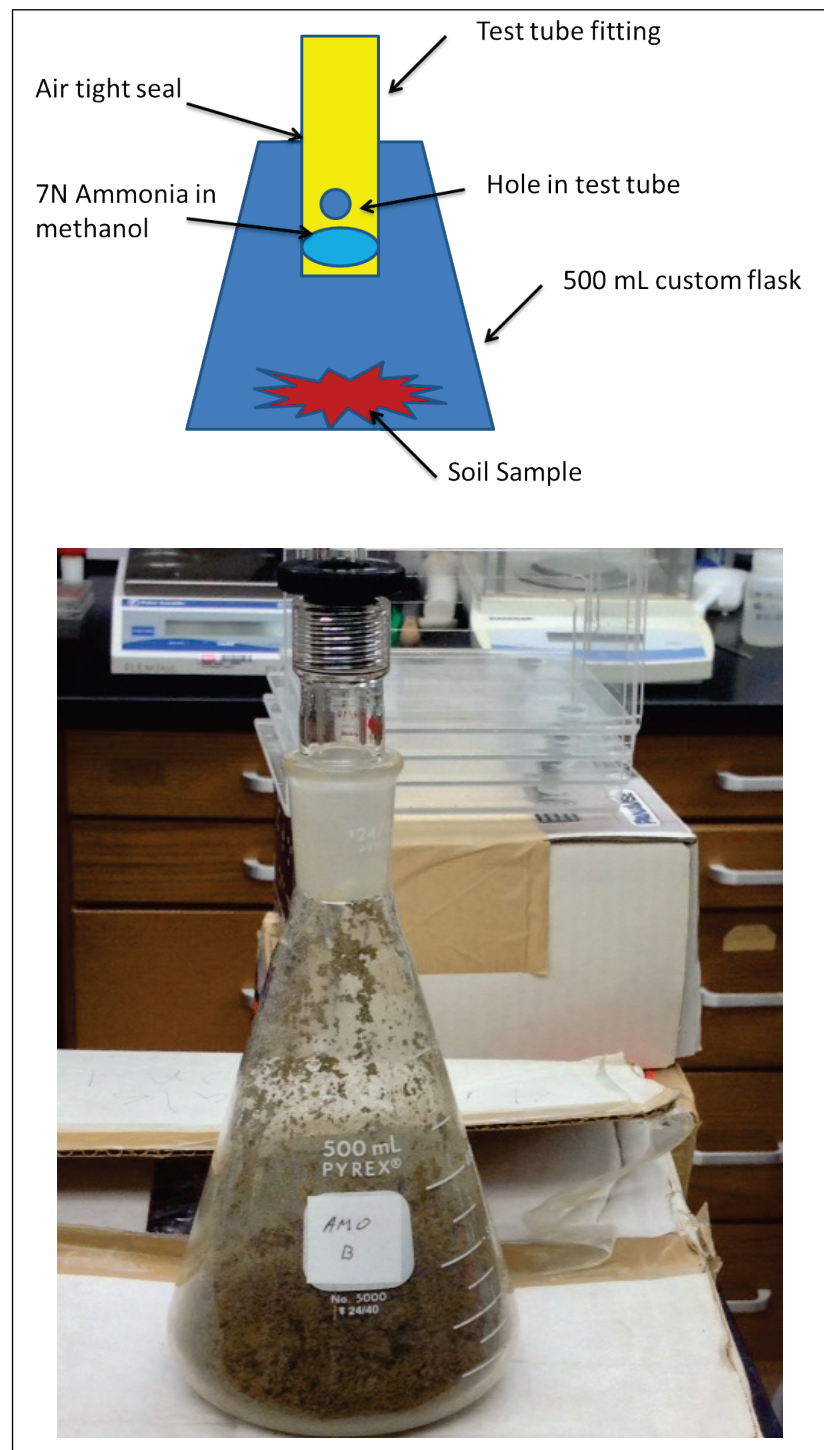
Exploration of ammonia oxidizing microorganisms

Figure 10 is a schematic and photograph of the experimental reactor used for this test. The reactor consisted of a 500 mL Erlenmyer with a ground glass neck joint. An adapter holding a center well with a side hole and an open top sealed with a septa closure Soil was charged with ammonia gas from the evaporation of 0.63 ml of 7 N ammonia in methanol placed in the center well. The flasks received 300 g of soil and 26 mL of deionized water to supplement the water content. Four reactors were set up. Three of the reactors were dosed with 7N ammonia in methanol, and the fourth reactor was dosed with an equivalent volume of methanol only.

As discussed in the experimental method for the treatment of halogenated propane, this method would result in a pH <9, which is not sufficient for alkaline hydrolysis. However, research on the stimulation of ammonia-oxidizing organisms is typically conducted within pH ranges that are not too far away from the neutral (i.e., usually at pH levels < 9), so keeping pH below the area of 9 was desired for this experiment.

The experiment was run over a 283-day period between 12/08/2014 to 09/17/2015, with sampling conducted roughly every 40 days. During sampling, the sample wells in the test tubes were recharged and the flasks were aerated. After 140 days (04/27/15), data indicated that ammonia levels in the flask were greatly elevated, so recharging of ammonia and control wells were discontinued. It was also decided at this time to open the flasks at the midpoint between sampling periods as a precaution against oxygen depletion.

Figure 10. Schematic (top) and photograph (bottom) of experimental apparatus.



Materials

Soils

Halogenated propane studies

Test soils for the chlorinated propane studies were provided from the Brown and Bryant Superfund Site in California – a site with deep vadose zone contamination with TCP, DCP, and other halogenated propanes. Soil cuttings (from a depth of approximately 15.2 m, or 50 ft) obtained during drilling operations within areas with suspected contamination were sent to the ERDC. Subsequent analysis of the soil cuttings indicated that contaminant levels were below detection limits. Soils were sieved (1 mm sieve) then homogenized using a tumbling, ceramic ball mixer (20 rpm for 5 days).

Explosives studies

Explosives studies were performed on a mixture of contaminated soils from two sources. The mixture consisted of 91.87 g from the former Sioux Army Depot (SAD) soil and 1000 g from the former Plum Brook Ordnance Works (PBOW) soil. Soil from SAD contained high levels of RDX and TNT, but was only available in a limited quantity. Soil from PBOW contained only high levels of TNT, but was available in larger quantities. Homogenization was obtained by tumbling in a ceramic ball mixer (20 rpm for 5 days).

The PBOW soil stock had been used for numerous studies in the past. Because it had been processed and mixed repeatedly; it was very fine. Even mixing in the SAD soils resulted in very fine soils for the experiment (Figure 11). This fineness was advantageous in terms of spiking and homogenization, but could have affected gas penetration.

Figure 11. Very fine, homogenized soil used in the explosives study.



Measurements

Soil moisture

Soil moisture (wet basis) was determined by direct heating according to ASTM D 4959.

Soil pH

The pH was measured using EPA Method 9045D (USEPA 2004), modified by the method of Kissel and Vendrell (2004), which stabilizes the measurement in a mild, 0.01 M CaCl₂ in deionized water solution (20 mL solution to 10 g of soil).

Nitrate, nitrite, ammonia

Nitrate, nitrite, and ammonia were extracted from soil using a 0.01M KCl solution (3 g of soil in 30 mL solution), as described in Turrion et al. (1999). Nitrate and nitrite were quantified using USEPA Method 300.0, Determination of Inorganic Anions by Ion Chromatography (Pfaff 1993). Ammonia was also analyzed by ion chromatography set up for cationic separation, using the method developed by Dionex (2001) (see Figure 12 for picture of ERDC's system).

Figure 12. Dionex ion chromatograph used for analysis of inorganic nitrogen species.



Total Kjeldahl Nitrogen (TKN)

TKN is a measure of organic nitrogen and ammonia. It was sent to Waypoint Analytical Mississippi, Inc. (Jackson, MS) for extraction and analysis using EPA Method 351.2.

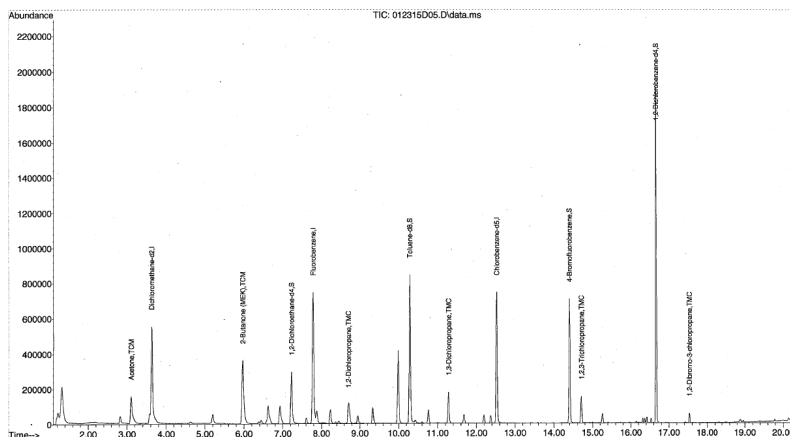
Halogenated propanes and chloroform

Sample collection, preservation, and shipping for halogenated propanes were based on email communication on 5 November 2013 between Mr. Scott Waisner of ERDC and Mr. Richard Bauer of EPA Region 9 Laboratory, and are consistent with EPA method 8260C for volatile samples. The procedures are outlined below:

- Approximately 5 mL of soil sample was added to a 40 mL VOA vial containing 10 mL of methanol.
- Tare weight (vial, cap, methanol, label) and total weight (includes soil) was recorded on the vial label and sample sheet.
- Vials were packed in a foam shipping cooler with ice and shipped via FedEx overnight.
- One trip blank of 10 mL methanol in a 40 mL VOA vial.

Analyses of halogenated propanes and chloroform used EPA Method 8260C (USEPA 2006) and were conducted by the EPA Region 9 Laboratory (Richmond, CA). These analyses followed Region 9's own QAPP (Laboratory Quality Assurance Plan for USEPA Region 9 Laboratory). The quantification limits in soils for the compounds was 120 ug/kg, except for 1,2-DB-3-CP, which was 500 ug/kg. A chromatogram of one of the analyses is shown in Figure 13.

Figure 13. A chromatogram from our studies from 8260C analysis of halogenated propanes.



Explosives

Explosives were extracted and analyzed in ERDC using EPA Method 8330 for explosives. Soils were extracted with acetonitrile according to section 2.5 of that method. Acid neutralization of the soil using this method is necessary prior to extraction to obtain the most accurate analyses for lime-induced alkaline hydrolysis and to account for any lime residuals (Larson et al. 2012). This was not necessary for this study, due to the differences in creating alkaline conditions (i.e., the reactive gas process does not leave unreacted, alkaline residuals in soil).

Ammonia oxidizing microorganisms

Ammonia-oxidizing microorganisms were quantified using quantitative polymerase chain reaction (qPCR) to enumerate the number of gene copies coding for ammonia-oxidizing activity. These analyses were performed by Microbial Insights of Knoxville, TN.

3 Results

Evaluation of pH increase via ammonia gas

Figure 14 summarizes the change of soil pH when the soil is exposed to a 5% ammonia gas mixture flowing through a 20 cm long x 2.5 cm diameter (8 in long x 1 in diameter) (See Figure 15 for experimental setup). The pH had a starting value of 7.5 in the column. The column was operated in an upflow manner, so the bottom of the column was the inlet. In the bottom portion, the pH increased to 9.6 at 250 scc, where the increase leveled off. The pH reached 10.3 after 1150 scc, and slightly above 10.5 after 2900 scc, which was the end of the experiment. Increases in soil pH in the upper portion of the column lagged behind those in the bottom of the column, but were approaching the same level near the end of the tests.

Figure 14. Increase in soil pH when exposed to a 5% ammonia gas mixture. The column operated in bottom-to-top flow.

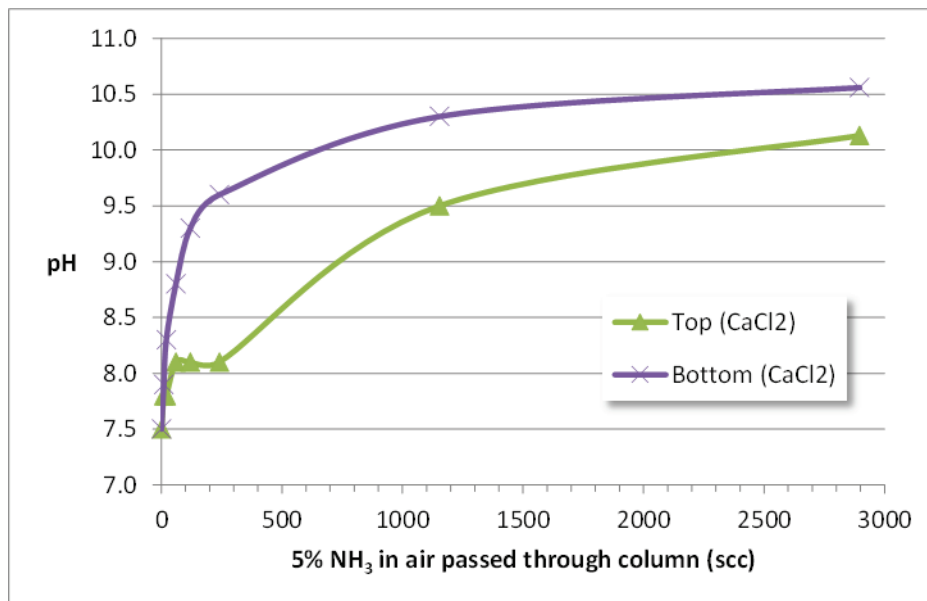


Figure 15. Ammonia gas experiment setup.



Treatment of halogenated propanes by ammonia gas induced alkaline hydrolysis

Two batch studies were conducted evaluating the degradation of halogenated propanes. The first study, Test 1, included chloroform as a co-contaminant, and was conducted at two temperatures, 23 ° and 65 °C. The initial soil pH had previously been measured at 7.8. Figure 16 summarizes the final pHs of the soils after the 14-day experiment. The pH of the control soils (23 ° and 62 °C) averaged 8.0 and 8.2, respectively. The ammonia-gas-treated soils had average pHs of 11.8 (23 °C) and 11.7 (62 °C). The pH increases were statistically significant ($\alpha < 0.010$).

Figure 16. Test 1 pHs after ammonia. Asterisks indicate statistically significant differences compared to controls ($\alpha < 0.010$).

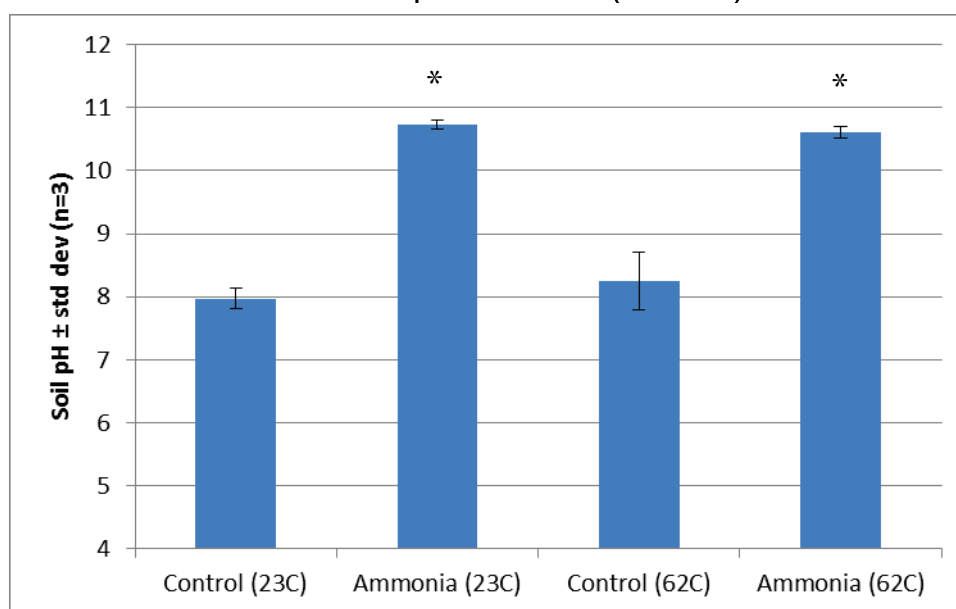
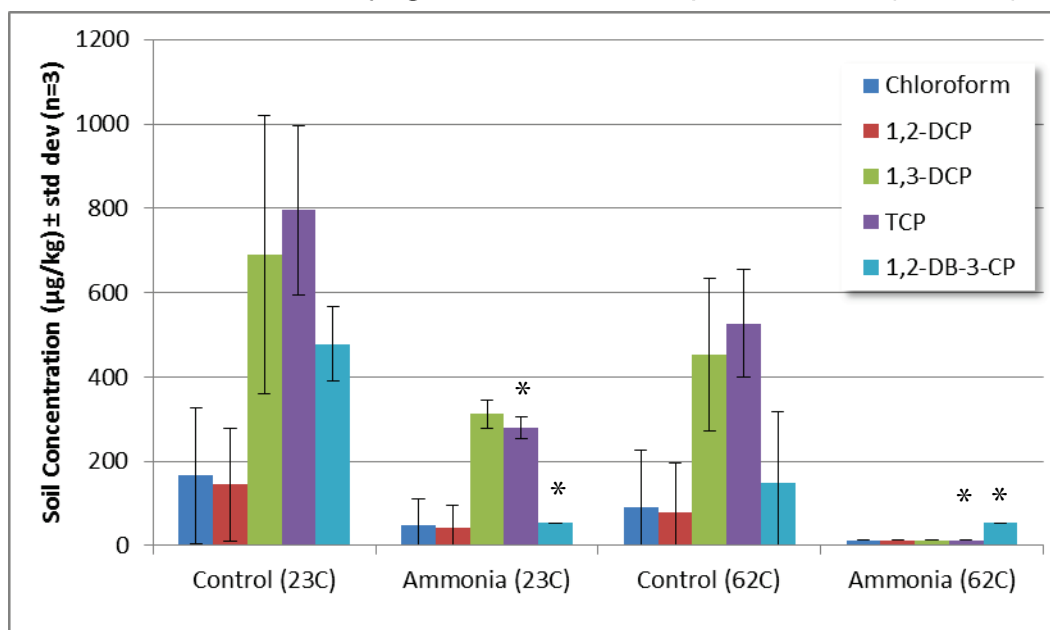


Figure 17 compares the final, average concentrations of the ammonia-treated reactors and the controls at 23 ° and 62 °C. The concentrations of chloroform, 1,2-DCP, 1,3 DCP, and TCP were below detection and reported at the detection limit. The concentrations of the ammonia-treated contaminants was less than that of the controls. In most cases, the decrease was statistically significant ($\alpha < 0.010$), but for chloroform and 1,2-DCP, the change was not statistically significant, primarily due to high variance in the initial concentrations. The TCP concentrations at 23 °C was 65% of the control and was at least 97% of the control at 62 °C.

Figure 17. Ending concentrations in Test 1 in control and ammonia-treated spiked soils. Asterisks indicate statistically significant differences compared to controls ($\alpha < 0.010$).

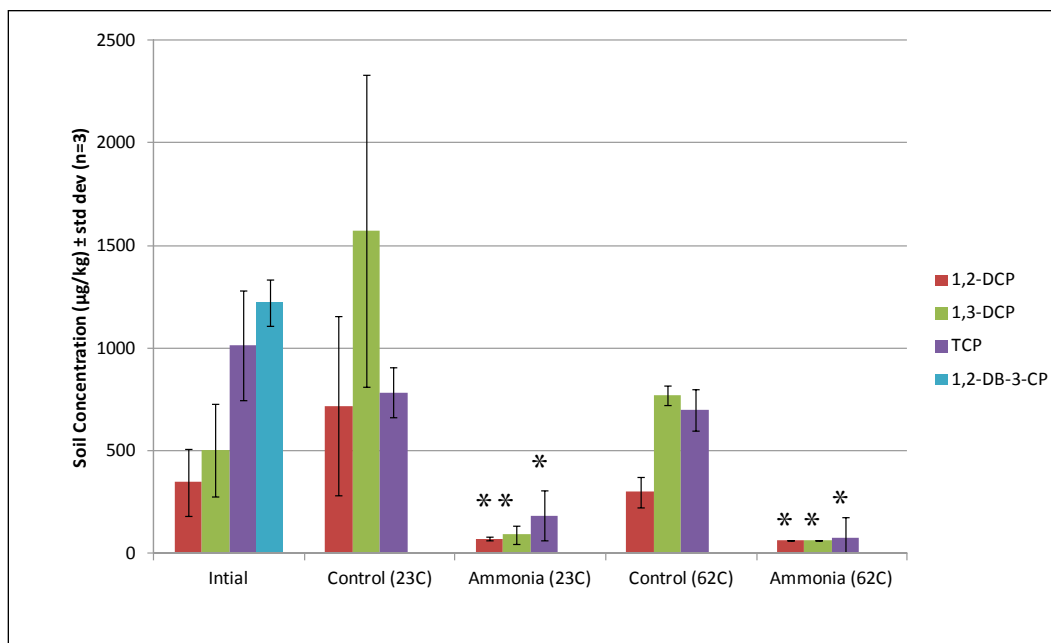


The results from Test 1 were promising, but there were some issues that necessitated a second test. First, the initial data was flawed, and the authors did not include it in the graphs. Second, some of the more volatile constituents (chloroform and 1,2-DCP, see Table 1) did not yield statistically significant results despite rather substantial removals. Test 2 endeavored to address these issues by more careful handling of the time 0 sample, removal of chloroform, which was determined to be too volatile to accurately test, from the chemical mix, and a higher spiking level of 1,2-DCP.

Figure 18 summarizes the results from Test 2. The results established statistically significant removal of 1,2-DCP at 23 ° and 65 °C, as well as reconfirming removal for 1,3-DCP and TCP. However, the test did have a confounding result in that DBCP was below detection limits in both the

ammonia-treated reactors and in the controls. TCP removal was 81.8% at 23 °C and 92.4% at 62 °C for ammonia-treated compared to 22.7% and 31.0% in controls.

Figure 18. Results of Test 2, evaluation of alkaline hydrolysis of halogenated propanes stimulated by ammonia gas. Asterisks indicate statistically significant differences compared to controls ($\alpha < 0.010$).



In each study, the contaminants were substantially removed. However, in both studies, the statistical significance of some of the contaminants was confounded. Combining the results of the two studies (as done in Table 5) demonstrates that alkaline hydrolysis by ammonia gas exposure accounted for contaminant removal in most cases, and all contaminants (except for chloroform) had statistically significant results in at least one of the two tests.

Volatility of the constituents was likely the cause of the lack of statistical significance for chloroform and 1,2-DCP in Test 1. These were the two most volatile compounds in our mixtures (Table 1). The loss of DBCP in Test 2 was less clear, and the team was not able to identify a convincing reason. DBCP was one of the lowest volatile of the constituents, so volatile loss seems unlikely, especially since more volatile constituents were not lost in the controls. Soil is an inherently heterogeneous matrix, and it can be very challenging to achieve completely uniform concentrations of contaminants, throughout a container of soil, via spiking and homogenizing. However, the initial values of this compound had the least variability (see initial error bars

in Figure 18), which argues against a spiking / homogenization issue. The chromatograms were manually reviewed to determine if there could have been a retention time shift, but no shifts could be identified. One possibility could be irreversible binding of the compound on soil, although it would be expected that the team would have seen a similar phenomenon on the first experiment.

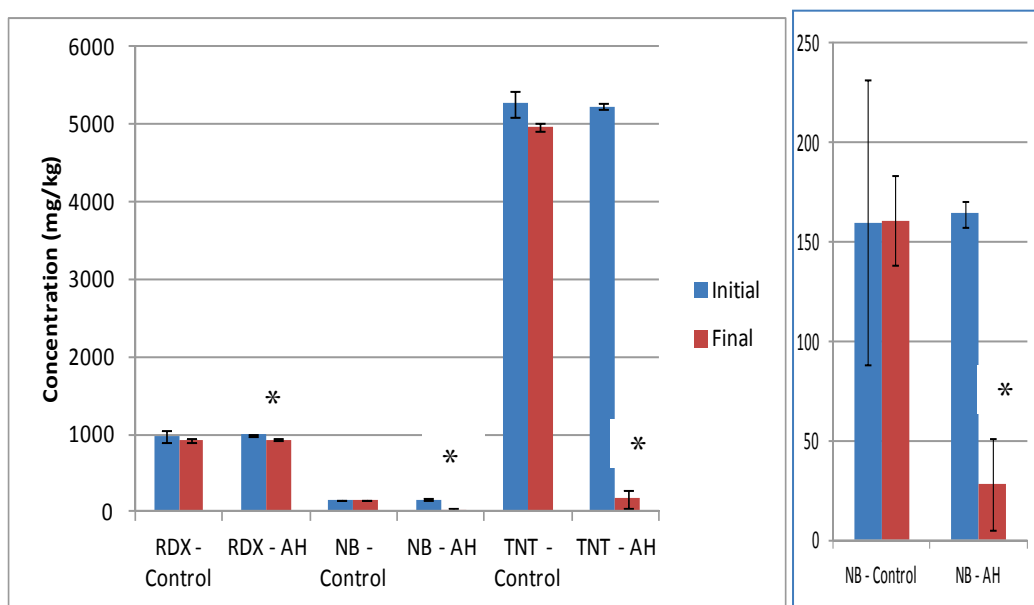
Table 5. Summary of confidence of change analyses for the two tests evaluating degradation of halogenated propanes. Asterisks indicate statistically significant differences compared to controls ($\alpha < 0.010$).

Confidence of a Change					
<u>Condition</u>	<u>Chloroform</u>	<u>1,2-DCP</u>	<u>1,3-DCP</u>	<u>TCP</u>	<u>1,2-DB-3-CP</u>
23C Test 1	80%	82%	92%*	99%*	100% *
23C Test 2		96% *	98% *	100% *	
62C Test 1	92%	94% *	99% *	99% *	100%*
62C Test 2		100%*	100%*	100% *	

Treatment of explosives by ammonia-gas-induced alkaline hydroxide

Figure 19 summarized ammonia-gas-induced alkaline hydrolysis of explosives in a mixture of PBOW and SAD soils. The soil mixture was relatively dry, with a moisture content of 2.6%. Three explosive compounds were investigated, RDX, TNT and Nitrobenzene (NB). None of the untreated controls showed substantial decreases in concentration, nor were any of these changes statistically significant ($\alpha = 10$). For ammonia-treated soils, TNT and NB had substantial decreases in concentrations (averaging 96% and 79%, respectively), and these decreases were statistically significant. RDX had a modest, 5% average decrease. The decrease was, however, statistically significant ($\alpha < 0.010$).

Figure 19. Results of the ammonia-gas-induced alkaline hydrolysis of explosives in soils. Nitrobenzene results are highlighted on the right. Asterisks show statistically significant differences ($\alpha < 0.010$).



Penetration of pH increasing reactions in a column study

Figure 20 shows ammonia and pH concentrations in the column following ammonia treatment. Initial concentrations of these constituents were relatively stable (see Figure 21 for more detail on initial ammonia concentrations). As expected, ammonia concentrations were highly elevated (over 1000 fold) in the initial 2.25 column segments. Eventually, by the 3rd segment, concentrations dropped to the approximate levels prior to treatment. Similarly, pH increased as ammonia concentrations increased in the soil, elevating from levels of around 7.8 to as high as 10.8. The pH elevation occurred through the first three segments, after which, as with the ammonia concentrations, the measurements leveled off. However, the pH was still slightly elevated compared to initial levels throughout the column.

Figure 21 summarizes concentrations of inorganic nitrogen species (ammonia, nitrite, nitrate) in the column before and after treatment by ammonia gas. Ammonia was elevated in the first 2.0 columns, with levels increased to more than 1000 times over the initial concentration of approximately 1 mg/kg. After the first two columns, the ammonia levels appeared to be lower than the initial concentrations. Nitrite concentrations initially averaged 0.8 mg/kg. After ammonia treatment, nitrite averaged 0.5 mg/kg, close to the initial level, but the variability increased.

Figure 20. The pH and ammonia measurements before and after ammonia gas treatment for the column flow through study.

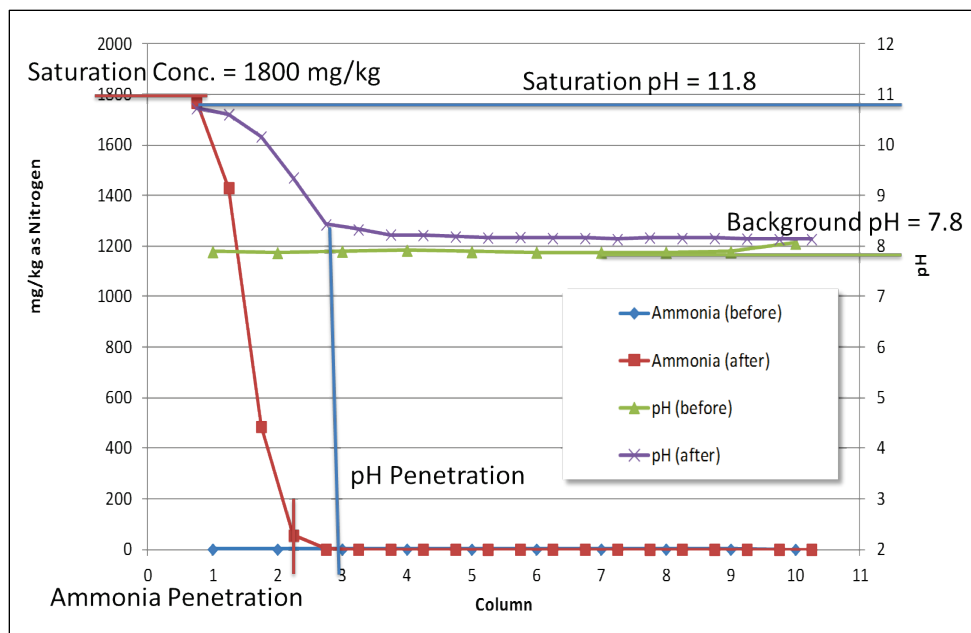
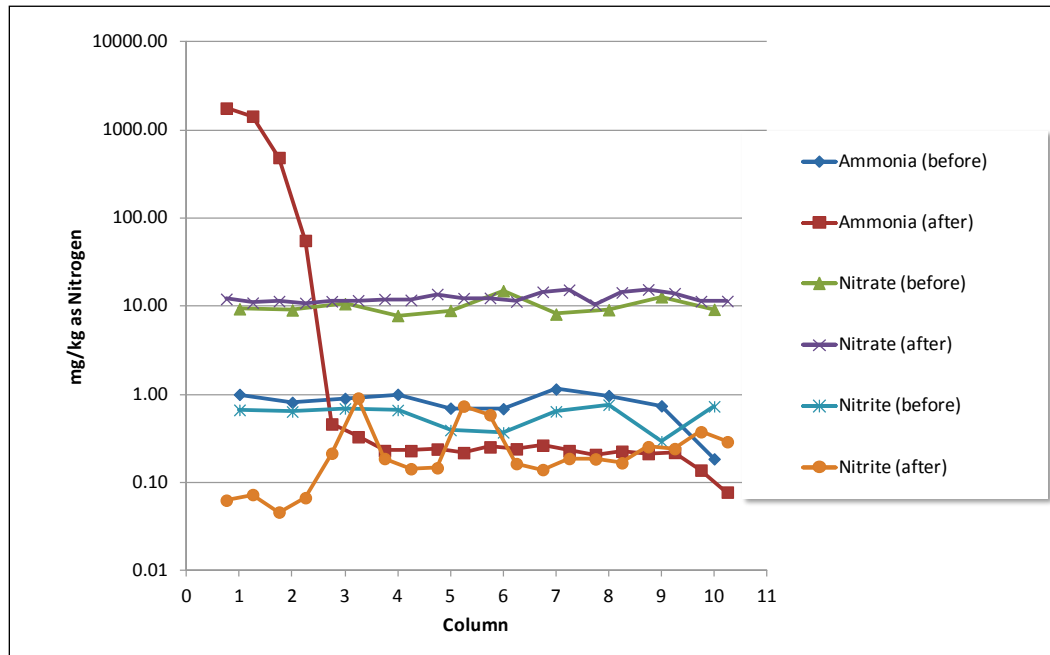


Figure 21. Concentrations of inorganic nitrogen forms during the seven-day column flow through study.



There was concern that prolonged movement of the dry gas mixture through the soil column might result in some moisture loss from the soil, so the soil moisture was measured in the column segments (Figure 22). The initial moisture content of the first nine column segments ranged from 12.4 to 10.9%, with higher levels on the inlet side, and lower levels toward

the outlet. The reason for the differences in moisture content along the length of the column was not clear. The last column segment, segment 10, which was filled with uncontaminated soil, had a considerably lower water content of 7%. After ammonia gas treatment, the water content ranged from 12.8 to 11.4% through the first nine columns, and once again moisture content remained higher toward the inlet and lower toward the outlet. And the last segment had a water content of 6.9%. Overall, there was no evidence of moisture depletion during the experiment.

Figure 22. Soil moisture profile in column segments before and after the seven-day study.

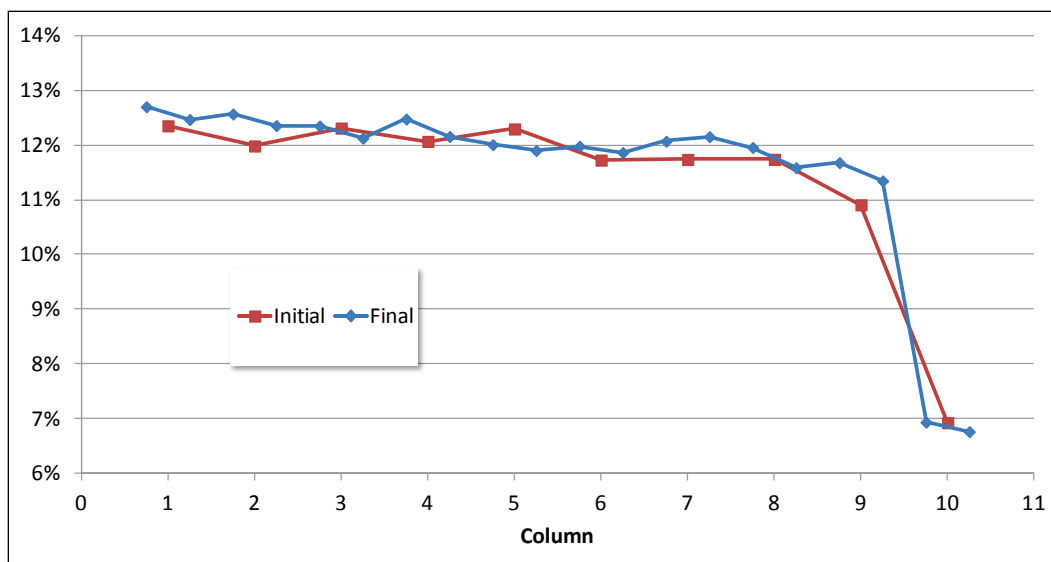
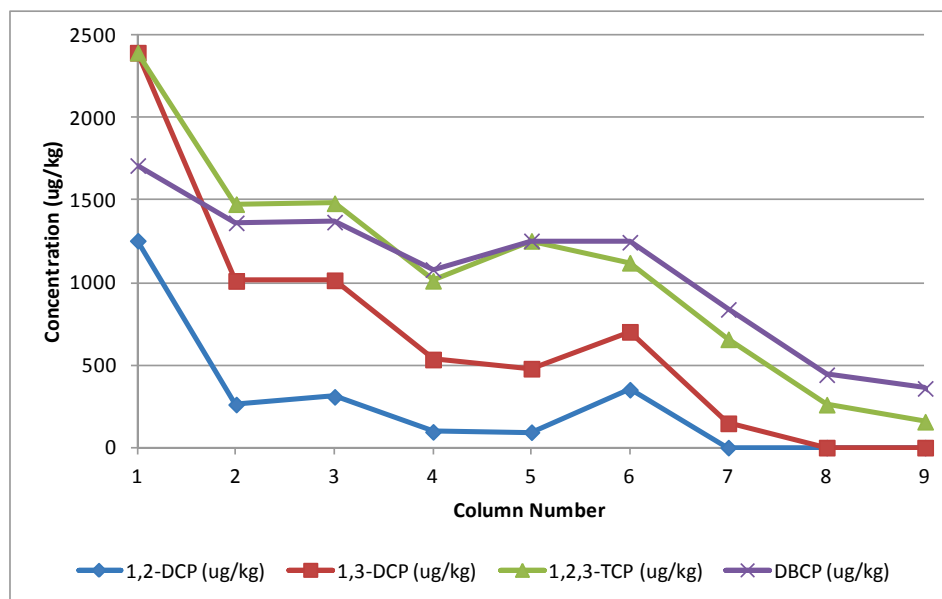


Figure 23 shows initial concentrations of the halogenated propanes in the 9 spiked-column segments (the 10th segment was not spiked). Initial contaminant levels were as high as 2400 ug/kg for 1,3-DCP and TCP. The initial contaminant levels were highest in the segments at the ammonia gas influent end of the column, and generally lower moving from the influent to the effluent segments of the column. This may have been related to volatile losses, since column 1 was filled first.

The post-treatment data from the column study indicated that the chloropropane concentrations in the soil samples (from 20 sub-segments) were below detection limits. The total, initial mass of contaminants present in the column were: 1,2-DCP 299.5 ug, 1,3-DCP, 795.2 ug, 1,2,3-TCP 1,241.2 ug, and DBCP 12,222.1 ug. It is likely that a significant amount of contaminant destruction occurred in the first three segments, where a substantial increase in pH was observed. However, the fact that contaminant levels were below detection limits in locations where no

change in pH was observed, indicates that at least a portion of the contaminant removal occurred due to volatilization (i.e., due to the “stripping” action of the gas moving through the soil column).

Figure 23. Spiked concentrations of halogenated propanes in segments used in column study.



After exiting the last column segment, the off-gas was routed through two sorbent tubes attached in series. The sorbent tubes contained a media to adsorb any contaminant mass that was volatilized during the column test. Data from the analysis of the sorbent tubes indicated the 1st tube captured 16.4 ug of 1,2-DCP and 2.4 ug of 1,3-DCP. The 2nd tube captured 1.7 ug of 1,2-DCP. The TCP & DBCP were not detected within either tube.

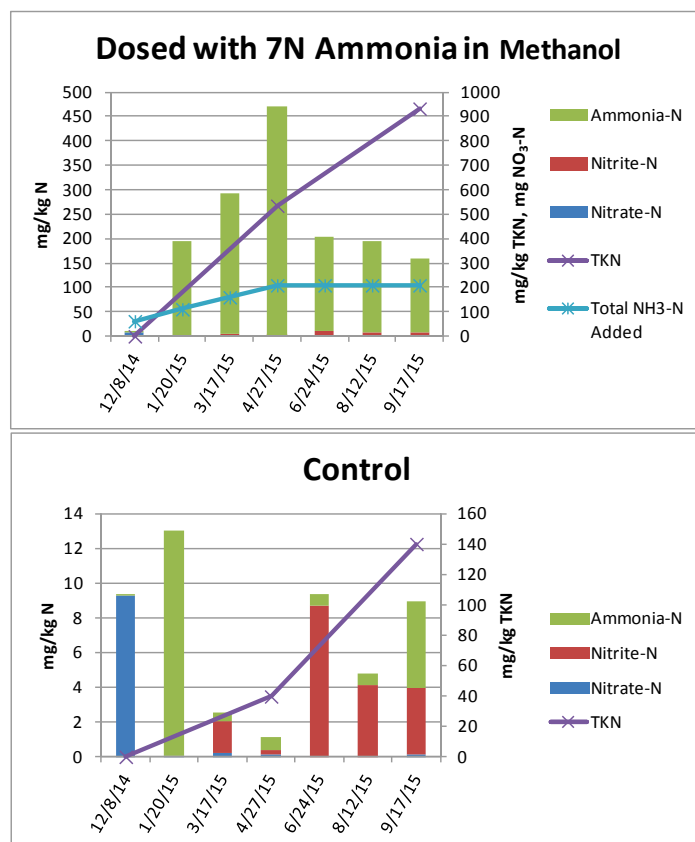
The approximate percentages of the initial mass recovered on the sorbent tubes was ~6% for 1,2-DCP, and ~0.3% for 1,3-DCP. It is not surprising that a significant mass of 1,2-DCP was recovered on the sorbent tubes, given that 1,2-DCP has a substantially higher Henry’s constant than the other contaminants. The sorbent tube data supports the case for contaminant destruction occurring in the soil columns, and that removal due to volatilization was limited.

Exploration of ammonia oxidizing microorganisms

Figure 24 summarizes inorganic nitrogen and TKN in the ammonia-gas-treated and control reactors during the experiment. Soil moisture was similar in both the control and the ammonia-treated reactors, increasing

slightly from 13.8% to 14.4% in the control and from 13.6 ± 0.1 to 14.5 ± 0.2 in the ammonia-treated reactors. The pH of the control ranged from 6.89 to 8.14 (the initial measurement), while it ranged from 7.35 ± 0.30 to 8.27 ± 0.04 in the ammonia-treated vessels.

Figure 24. Results of nitrogen-forms concentrations in the ammonia-oxidizing microorganisms study.



The ammonia-treated soil, as expected, had substantial increases in ammonia concentrations as the experiment progressed. And although both the control and experimental reactors had increases in TKN, the increase in the experimental reactor was tenfold that of the control. The TKN increase in both reactors suggested that some microbial growth was occurring during the experiments.

The results from the ammonia monooxygenase gene assay were essentially non-detect during the 283-day study (Table 6). However, a significant increase in nitrite was observed in the ammonia-treated reactors in the last three sampling points. This may indicate some ammonia oxidation was occurring, but that it did not result in sufficient growth to be detected by the qPCR assay.

Table 6. Numeration of ammonia monooxygenase gene copies.

Date	Days	Control	Ammonia Treated
12/08/14	0	<10 ⁴	<10 ⁴
01/20/15	43	<10 ⁴	<10 ⁴
03/17/15	99	<10 ⁴	<10 ⁴
04/27/15	140	<10 ⁴	<10 ⁴
06/24/15	198	<10 ⁴	<10 ⁴
08/12/15	247	<10 ⁴	<10 ⁴
09/17/15	283	<10 ⁴	<10 ⁴

4 Discussion

pH Elevation

The pH elevation associated from flow-through column tests appeared to occur relatively quickly with ammonia gas addition. The elevation was greater in the initial part of the column for all the data presented, suggesting that the small columns never quite reached saturation. The pH levels as high as 10.8 were measured.

Relating the pH to soil buffering capacity could be useful for determining how much ammonia gas would need to be injected to achieve a target pH level for a specific soil type. Kissel et al. (2012) indicates that for the soils studied, the lime buffering capacity (LBC) ranged from 100-500 mg $\text{CaCO}_3/\text{kg/pH unit}$ ($\text{LBC} = 100\text{-}500 \text{ mg CaCO}_3/\text{kg/pH}$). The team modified this term into an "ammonia buffering capacity" (ABC) estimate based on the relationship that 2 moles of NH_3 is equivalent to 1 mole of lime ($\text{Ca}(\text{OH})_2$), in terms of quantity of protons neutralized:

$$\text{ABC} = \text{LBC} \times (17 \text{ g/mol NH}_3 / 100 \text{ g/mol CaCO}_3) (2 \text{ mol NH}_3 / 1 \text{ mol CaCO}_3) = 34\text{-}170 \text{ mg NH}_3/\text{kg/pH unit}$$

For example, if soil pH = 7.0, estimate the range of NH_3 required to raise the pH up to 10.0? Using the above ABC, and neglecting any side reactions: $3 \times (34\text{-}170) = 102\text{-}510 \text{ mg NH}_3/\text{kg soil}$.

There are some potential confounding factors. Side reactions could include reactions with constituents such as organic matter, clay, or cation exchange complexes. Reactions with soil moisture should exert an increase in pH, which would be different than side reactions that would exert NH_3 demand, without impacting pH.

Furthermore, Kissel et al. (2012) is based on use of LBC for acidic soils that only need to have the pH raised up to the neutral area (and it is based on an underlying, linear titration curve from pH 4.5-6.5). The team's situation is different, because the team members can only speculate on the shape of the titration curve as the pH increases beyond 6.5. A modification

of the LBC with a higher pH endpoint may be the basis for a useful predictive test.

Temperature effects in treatment of halogenated propanes

The studies of the treatment of halogenated propanes provided important, proof-of-concept confirmation of the reactive gas process's feasibility. When the results of the batch and column experiments were combined, data were generated indicating that each of the contaminants could be removed using this novel treatment process. However, there were also some confounding and anomalous results. The volatility of the contaminants tested and heterogeneous distribution of contaminants in the spiked soils probably contributed to the problematic results. The relationships between the controls and the ammonia-treated soils nonetheless confirm the viability of the reactive gas process for treatment of halogenated propanes.

Prior to initiating the laboratory work, and based on literature references, it was hypothesized that an elevated temperature would be necessary for effective treatment. Surprisingly, the results indicated that substantial removal could be achieved at room temperature. That said, increasing the temperature to 65 °C resulted in complete removal (below-quantification limits given in the Materials/Methods section) of the contaminants.

Providing heat to the subsurface can be accomplished by several techniques. Electrical resistance heating is probably the most commonly applied in situ thermal treatment process for chlorinated solvents, but steam injection has also been used at some sites. Radio frequency heating and thermal conductive heating have been demonstrated to effectively raise soil temperatures to comparable levels (Price et al. 1999, Stegemeier and Vinegar 2001). For moderate heating of the vadose zone, positive displacement blowers could be used (see Appendix 3 for calculations). However, it still is not entirely clear if any thermal enhancement will be necessary for field-scale implementation of the reactive gas process.

The limited approach of the study did not make it possible to accurately measure kinetic rates. However, it seems reasonable to hypothesize that the higher removals found at the higher temperature (62 °C) is related to faster kinetic rates. A study to elucidate kinetic rates and Arrhenius constants would be very worthwhile.

Soil moisture effect in treatment of explosives

Alkaline hydrolysis of explosives is a well-established remediation method for soil and groundwater. In this study, the team found that ammonia gas can elevate pH levels in soil sufficient for alkaline hydrolysis of most explosives. The data exhibited greater than 95 percent removal of TNT and of NB. RDX, on the other hand, had modest, but statistically significant removal with ammonia treatment.

Unfortunately, funding constraints for the explosives study did not permit an expanded investigation into the factors that contributed to the lower level of RDX removal. However, two factors may have contributed, kinetic rate and differences in contaminant availability in the water phase.

It is established that kinetic removal rates of RDX due to alkaline hydrolysis is slower than that of TNT, but there is a question of how slow. Early reports suggested that the difference was not great, with the first order rate constant for TNT degradation in water 0.23/hr, compared to 0.18/hr for RDX (summarized in Larson et al. 2012). Similarly, treatment half-lives in similar soils for TNT and RDX are relatively close as well 0.15/day vs 0.28/day, respectively. However, Larson et al. 2012 demonstrated that residual lime in the contaminant extraction phase can lead to misleading degradation interpretation. More recent work (Felt, Personal Communication, 2016) suggests that RDX degradation is very slow, at levels lower than pH 11.5. The team was able to elevate the pH to about 10.8, so it was lower than the ideal range for RDX degradation.

However, in another project using the same soil (SAD), RDX degradation greatly lagged behind that of TNT, even though pH levels were elevated above 11.5 (Felt, Personal Communication, 2016). This suggests that contaminant availability is also a factor. The team hypothesizes that this could be related to water content. Alkaline hydrolysis is a reaction that occurs in the solution phase. The application of alkaline hydrolysis of soil contaminants consists of two steps, dissolution of the contaminant in the soil moisture, followed by its degradation. At this time, the alkaline hydrolysis treatment has been largely limited to excavated or near-surface soils. In these applications, water is often added to increase contaminant dissolution, and to compensate for low-moisture content in soils. Water addition may also be necessary to compensate for addition of dry reagents (e.g., lime, or sodium hydroxide), which can withdraw moisture from the

soil. Water contents of 20 to 30% are commonly achieved and can be higher for slurry phase applications (Medina et al. 2007).

For ammonia gas application to deep vadose zone, the addition of moisture would probably be accomplished through injection of humidified air. Obviously, steam would provide both heat and moisture, but this discussion will focus on moisture only. In shallower applications, it may be possible to leach water into the treatment area, but this approach would be problematic for deeper applications, due to channeling, and it could promote leaching of contaminants.

In the case of the explosives-contaminated soils, the water content was 2.6%. The team hypothesized that this low water content, coupled with the lower RDX kinetic transformation rate and lower water solubility (~28 mg/L compared to ~125 mg/L for TNT), resulted in a lower removal percentage as compared to TNT and NB.

The RDX results indicate that the effect of water content should be considered in applying ammonia treatment to dry soils. The encouraging aspect of these studies is that lower moisture contents did not appear to have too much of an effect on the removal of TNT and NB.

Discussion of column results

For pH and ammonia, the team saw a modified form of a penetration curve. The samples near the gas influent had elevated pH levels and concentrations of ammonia (close to pH 11 based on the small column studies). These elevated levels penetrated up to the 5th sampling point, after which little or no elevation was found. Since each sampling point represented a 10 cm (4 in.) midpoint, the total penetration was 50 cm (20 in.) during the seven-day experiment. The authors hypothesize that if they continued to load ammonia, the penetration would continue.

However, in a well injection, the radial geometry results in a dissipation of injected constituents. Newell et al. (2013) studied the injection of helium gas in soil, and determined a radius of influence of 15 ft (4.6 m). This distance was at least two times greater than what they estimated could be achieved by the injection of water (assuming a substrate like molasses or permanganate). In studies in which hydrogen and propane were injected into the subsurface, they found evidence of oxygen depletion at distances up to 40 ft (12.2 m).

The nearly complete removal of the contaminants during the spiked soil column study was unexpected. However, it shouldn't be surprising that recently spiked contaminants would be relatively easy to move from the sorbed phase, into the aqueous phase (of the soil moisture), where they would be available for alkaline hydrolysis reactions. Aging of contaminated soils would probably decrease the contaminant removal efficiency of this process.

The data from the sorbent tubes indicated that volatilization of contaminants was limited. These results also suggest that the process could be applied to the subsurface for in situ destruction, while at the same time, limiting the extent of contaminant displacement due to gas injection. Contaminant displacement would be a greater concern for contaminants with a high vapor pressure (e.g., 1,2-DCP), and a lesser concern for contaminants such as 1,2,3-TCP and DBCP.

Stimulation of biodegradation

Effect on soil nutrients

Many studies on biodegradation have indicated that the addition of nutrients (nitrogen, phosphorus, and micronutrients) can stimulate faster and more complete treatment for many organic contaminants, because petroleum based products are hydrocarbons (and essentially devoid of nitrogen and phosphorus). The addition of nutrients is still commonly used to stimulate biodegradation. Nutrients are typically added by dissolving them in water. This can be easily done ex situ in landfarming or slurry reactors. It can also be accomplished for relatively shallow contamination in situ or in groundwater. Addition of nutrients to the deeper vadose zone is more difficult. For deeper vadose zone applications, the reactive gas process may offer a novel approach for targeting delivery of nitrogen to discrete locations.

Ammonia-oxidizing microorganisms

As discussed in the introduction, there was an interest in these organisms since AMO has been linked to co-metabolism of chlorinated solvents (Vannelli et al. 1990). However, the team did not find any measureable increase in gene copies coding for AMO. Stark and Firestone (1995) found active ammonia oxidation in an ammonia-gas-treated soil. Okano et al.

(2004) observed increases in ammonia oxidizing bacterial genes (on the order of a factor of 10) in a 28-day study.

It is not entirely clear why an increase in AMO gene copies was not observed during the AMO study. One possibility is pH. Frijlink et al. (1992) found that growth and metabolic activity of ammonia oxidizing organisms decreases dramatically when the pH is less than 7. Frijlink et al. studied a pH range from 5 to 8, and found that activity was best expressed at a higher pH. Sato et al. (1985) studied growth of a nitrifying bacteria (*Nitrosomonas europaea*) with a test medium at 8.5. During the AMO study, the pH levels were slightly higher than these ranges, on the order of 8.8, so it is possible that there could be a pH limitation on activity. However, their study did not show an actual limitation, and our pHs were less than 9.0, a level that is usually considered a non-restrictive pH level. Inhibition due to pH does not appear to be a satisfactory explanation.

Another possibility is that competitive respiration limited AMO activity. The ammonia was added as a mixture with methanol. Methanol is a readily biodegradable compound and a good carbon and energy source for microorganisms. Ammonia oxidation is an autotrophic reaction in which energy from the reaction is used to fix carbon dioxide. Also, microbial ammonia oxidation requires oxygen. Heterotrophic microorganisms are generally thought to have a competitive advantage over ammonia oxidizers. A rapid increase in the population of methanol degrading heterotrophs could have depleted oxygen within the pore-space of the interior regions of the soil, thereby limiting growth of ammonia oxidizers.

As indicated above, oxygen content could be a factor. The oxygen content in the headspace of the reactors was calculated, and there should have been an excess amount of oxygen for metabolism of the methanol. Still, it is possible that some degree of oxygen depletion occurred within the pore space of the interior regions of the soil. The last time that ammonia-in-methanol was added to the flasks was in mid-March, and incubation of the soil continued for another six months. If the methanol was metabolized relatively rapidly (as expected), then the hypothesized depletion of oxygen in the pore space of the interior regions of the soil would have only been temporary. And it was expected that there still should have been time for AMO activity to become established.

Literature references seem to suggest that ammonia oxidation should have occurred to a much greater extent than was observed during the AMO study, in spite of the added methanol. For example, ammonia oxidation is commonly observed in organic-rich, agricultural soils (Burger and Jackson 2003, Okano et al. 2004). Also, a field study evaluating a variety of respiratory reactions in estuary sediments found that ammonia oxidation does occur in organic-rich sediments and even in sediments approaching anoxic conditions (Eggleson et al. 2015). However, the redox conditions of topsoil can be very complex, and localized microsites exhibiting reducing conditions can be interspersed with microsites exhibiting oxidizing conditions. Also, oxidizing microsites may be associated with plant roots. One difference between the AMO study and a field site, is that there obviously were not any plant roots to supply oxygen to the interior regions of the soil in the flasks. Also, the soil used for the AMO study did not have the typical structural features that are usually present in top soil. Structural features such as cracks, worm holes, and hollow stalks from dead vegetation were also obviously not present.

Another factor could have been moisture content. Stark and Firestone (1995) found that nitrification readily occurred in moisture-rich soils, but dropped off in drier soils. The soils used in the study had moisture levels on the order of 12%, a percentage certainly on the drier side. However, significant water was added before the study, and the soils appeared to stay moist throughout the study.

Probably the most likely issue was simply that the soils, being relatively deep cores on the order of 15.2 m (50 ft) did not have an active AMO population. Therefore, AMO activity was greatly subdued. The Microbial Ubiquity Theory states that all soils contain at least traces of all metabolic processes, they simply need to be stimulated. In this case, the activity may have been minimal, and the 283-day experimental time may not have been enough for this population to grow to a point of being detected. However, there was some evidence of nitrite increases late in the experiment. This may have been a precursory sign of activity.

Contamination of groundwater by ammonia or nitrate

One potential drawback of the treatment scheme is that the addition of nitrogen in the subsurface could result in groundwater contamination. Nitrite and nitrate all have regulatory levels in drinking water, and ammonia is regulated in surface water (Table 7). Ammonia can be a

groundwater contaminant; however, it is not very common. The positively charged ammonium ion tends to adhere to negatively charged soil particles in the vadose zone, and negatively charged sediments that compose the matrix of the saturated zone. Thus, movement of ammonium ions in groundwater is minimal. Nitrite can also be a contaminant, but nitrite is often further oxidized to nitrate. Nitrite is usually present at only a very small fraction of the nitrate concentration, such that the concentration is usually insignificant.

Table 7. Regulatory limits for inorganic nitrogen species in water.

Compound	Type of limit	Level
Nitrate	MCL	10 mg/L as N
Nitrite	MCL	1 mg/L as N
Ammonia	Aquatic Life Criteria (USEPA 2013)	Time-weighted averages that vary based on pH and temperature.

Nitrate, on the other hand, is a much more common contaminant. High nitrate levels in groundwater are common in areas with extensive agriculture due to application of nitrogen fertilizers. The reactive gas process utilizes a mixture of ammonia in air, and the ammonia concentration in the gas is relatively low (i.e., 5-10%). In order to be converted to nitrate, the ammonia would first have to be oxidized. Although this is thermodynamically favorable, this reaction can be slow. Slow reaction was supported by the results from the AMO study, which had minimal oxidation of ammonia. However, the reaction rate will be impacted by site-specific conditions, and the microbial community — and can vary from one site to another.

An important aspect of trying to assess the risk of the reactive gas process to create the potential for nitrate is to consider the capacity of soil to adsorb ammonia. A great deal of research has been conducted regarding application of anhydrous ammonia (i.e., 100% ammonia, in liquid form) to topsoil. It is known that ammonia can sorb, or react, with various compartments within soil (e.g., moisture, organic matter, clay constituents, and cation-exchange complex). Studies have also shown that ammonia may compete with water for adsorption sites within soil. However, application of relatively low concentrations of ammonia gas to soil is a topic- area that is much less well understood. If the amount of ammonia introduced through the reactive gas process does not exceed the ammonia adsorption capacity of soil, then the reactive gas process would

not be expected to lead to nitrate contamination of groundwater. Differences in soil properties (e.g., buffering capacity) would need to be taken into consideration as to the site-specific nature of the ammonia adsorption capacity.

After ammonia sorbs onto soil, or reacts with pore water, it can be metabolized by microorganisms in a number of different ways. Depending on redox conditions; the presence of biodegradable organic matter; concentrations of oxygen, carbon dioxide, methane, and a host of other factors, ammonia may be transformed into nitrite, nitrate, nitrous oxide, nitrogen gas (N_2), and/or incorporated into microbial biomass. Any ammonia that becomes transformed into N_2 would essentially be removed from the system, and would no longer be available for nitrate generation. If the zone where the reactive gas process is being applied is well above the water table, then there would be an additional “buffer zone,” which would be available for adsorption and transformation reactions, before it would be possible for nitrate to reach groundwater. If the treatment zone is immediately above the water table, then there would be a greater potential for the process to have an undesirable impact on groundwater. Thus, although ammonia-gas treatment could create the potential for nitrate contamination in groundwater, a number of factors must be taken into consideration to properly assess the risk.

5 Conclusions

- Ammonia gas (5% ammonia-in-air) was effective at increasing soil pH to levels up to 10.8, sufficient for alkaline hydrolysis reactions to occur for the tested contaminants.
- Ammonia gas was used to raise pH of soils spiked with several halogenated propanes (TCP, 1,2- DCP, 1,3-DCP, 1,2-DB-3-CP). All were effectively treated. Chloroform was also removed, but confounding volatile removal made it impossible to statistically confirm alkaline hydrolysis treatment.
- Increased temperature (62° C) resulted in greater removal halogenated propanes. However, effective treatment occurred at 23° C.
- Ammonia-gas treatment was used to stimulate substantial and statistically significant removal of TNT and NB. RDX removal by ammonia treatment was minimal, but statistically significant.
- A soil column study showed penetration of ammonia, a substantial distance into the column, resulting in penetration of pH increase.
- Analysis of sorbent tubes from the soil column study indicated that only very limited displacement of halogenated propanes occurred due to ammonia gas injection. A limited degree of displacement occurred for 1,2-DCP, but there was no measurable displacement for TCP.
- A long-term, AMO study (using lower levels of ammonia) indicated significant increases in ammonia concentrations, with limited transformation of ammonia into nitrite. Nitrate did not increase.
- Decreases in ammonia, coupled with increases in TKN, indicated that ammonia served as a readily assimilated form of nitrogen, and that ammonia gas can be used to stimulate biological activity.
- The use of qPCR did not find any increase in ammonia-oxidizing microorganisms over 283 days. However, a small increase in nitrite could suggest some preliminary activity was occurring.

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Appendix A: Experimental Plans used in this Project

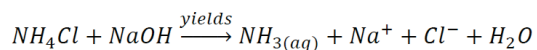
Production of Ammonia Gas in Jars

Materials

- Ammonium chloride
- Sodium hydroxide pellets
- Deionized water
- 40-mL VOA vial with septa cap
- Luer-lock hypodermic needle, 1-1/4 inch or shorter and 18 gauge or larger diameter suggested
- Luer-lock syringe, 3 or 5 mL capacity suggested

Procedure

1. Add 6.69 g of NH_4Cl to a 40-mL VOA vial.
2. Add 5.0 g of NaOH to the same 40-mL VOA vial and seal the vial with the cap.
3. Using a syringe and needle add approximately 1 mL of DI water to the vial through the septum. This will facilitate a rapid reaction between the two chemicals.
4. Remove the syringe from the needle and seal the vial with needle in the jar so that the vial will remain in a relatively upright position.



This will yield aqueous ammonia; however, since the volume of water is very small and the solubility of ammonia in a high pH solution is very low, almost all of the ammonia is released to the gaseous phase.

AMO Study Plan

Prepared by Victor F. Medina, Ph.D., P.E.

Purpose: The purpose of this study is to determine if ammonia gas addition can stimulate the production of ammonia monooxygenase (AMO) activity, an enzyme that oxidizes ammonia to hydroxyl amine as an autotrophic reaction. This enzyme has been demonstrated to co-metabolize a number of recalcitrant contaminants including trichloroethene. This study is preliminary in nature – the goal being to determine if such a reaction occurs within a time from just over 8 months. Our previous work has shown that ammonia gas is effective at raising soil pH, and that this can stimulate alkaline hydrolysis degradation of chlorinated propanes and explosives (TNT, RDX and nitrobenzene).

Plan

1. We will use soils that were collected from the Brown and Bryant Superfund site. An amount sufficient to complete the experiment will be prepared and homogenized via 72 hour tumble with ceramic balls. (Note: this soil preparation has already been initiated).
2. The experiment will be set up on 1 December 2014. If there is an unexpected issue, it will be set up as soon as possible afterwards.
3. The experiments will be set up in 1 L glass flasks with tube inserts that allow us to suspend vials of ammonia and methanol or just methanol above the soil. 300 g homogenized soils will be added to these four of these flasks.
4. Water will be carefully added to each flask to bring the moisture content to 15%. (The native water content in these soils is approximately 9%).
5. Background samples will be collected for AMO, Moisture content (gravimetric), pH (extraction in DI water and meter measurements), NO₃ (Ion Chromatograph [IC]), NO₂ [IC], NH₃ [IC], and TKN (send to contract lab via the chemistry branch).
6. Based on the study conducted by our GEMS student, the background pH of the soil is approximately 8.6. When 0.378mL of 7N ammonia in methanol was added to the suspended test tube, the resultant pH of the soil was on the order of 9.17. We will use that dosing for this experiment to prepare 3 test reactors. To account for the larger soil mass, the dosing will be 0.630mL.
7. A control reactor will be identically prepared, with a dosing of 0.0.630 mL of methanol (with no ammonia) in the suspended test tube.
8. The reactors will be sampled every 42 days according the schedule provided in table below through 21 September. This will encompass 6 events (not counting baseline). The sample will consist of 10 g for AMO measurement, 5 g for

moisture content and 5 g for pH. (120g total). Two extra AMO samples are available to reanalyze if there are confusing results.

9. The reactors will be respiked with 7N ammonia in methanol if the pH of 2 of the 3 test reactors reach or fall below 8.75 (0.1 pH units above background based on the preliminary study). The MC will be modified if the water content reaches or falls below 10% in at least 2 of the test reactors.

Date			Days		Weeks		Number of Soil Flasks		Number of Samples	
1-Dec		Day 0 / Baseline			0		4		4	
12-Jan		42	42		6		4		4	
23-Feb		42	84		12		4		4	
18-May		42	126		18		4		4	
29-Jun		42	168		24		4		4	
10-Aug		42	210		30		4		4	
21-Sep		42	252		36		4		4	
							additional samples (duplicates)		2	
							Total Number of Samples:		30	

The sampling schedule can be changed if preliminary results suggest a modification would yield better results.

10. On every other sampling date (84 days) we will take additional samples for NO₂, NO₃, ammonia and TKN. We anticipate each of these efforts to consume 30 g of soil in 4 events, or 120 g. Therefore, the sampling should consume 240 of the 300 g of soil.
11. Results will be prepared in tables and graphs to allow for efficient data analysis. We will apply the variation of the experimental reactors and assume the same would occur in multiple controls to determine statistical significant.

Extraction of Exchangeable Inorganic Nitrogen from Soil for Analysis by Ion Chromatography

Materials

- 0.01-M KCl solution
- centrifuge tube
- syringe and cannula
- 0.45- μ m glass-fiber syringe filter
- sample vial
- aluminum drying pan
- tube rotator

Procedure

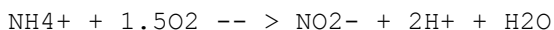
1. Collect soil sample and place in tared centrifuge tube.
 - a. Collect soil sample and determine moisture content.
2. Add 10 mL of dilute KCl solution to the centrifuge tube for each gram of soil added.
3. Place centrifuge tube on rotator for at 30-60 minutes.
4. Centrifuge sample or allow to settle.
5. Withdraw supernatant with syringe and cannula.
6. Filter sample with syringe filter and collect filtrate into sample vial.
7. Store extract at 4°C until analyzed.

Based on "Nitrogen–Inorganic Forms" in *Methods of Soil Analysis. Part 3. Chemical Methods*—SSSA Book Series, No. 5, Chapter 38. 1996. Soil Science Society of America and American Society of Agronomy.

Appendix B: Calculation of Oxygen Depletion Due to Ammonia Addition in AMO Experiments

If we add 0.630ml of 7N NH₃, this would equate to ~79mg of NH₄

Stoichiometry: 1.5 mole of O₂ consumed per mole of NH₃/NH₄ oxidized



If NH₄ = 79 mg, how much O₂ would be consumed?

NH₄ = 18 g/mol; O₂ = 32 g/mol

$79 \text{ mg of NH}_4 / (18 \text{ mg/mmol}) * (1.5 \text{ mol O}_2) / (1 \text{ mol NH}_4) = 6.6 \text{ mmol O}_2$

Determine volume of O₂:

$6.6 \text{ mmol O}_2 / 22.4 \text{ mmol/ml} = 0.3 \text{ ml}$

Volume of O₂ in 1 L of air (air=21% O₂) = 210 ml

Determine initial / final headspace O₂ concentration:

$$210 - 0.3 = 209.7 \text{ ml O}_2$$

Initial O₂ = 21.00%; Final O₂ = 20.97% (no significant change)

Appendix C: Soil Heating by Blower Calculation

Soil Heating Calculations				
ambient air temperature		70 deg F	21.1 deg C	
blower exhaust temperature		180 deg F	82.2 deg C	
delta T (heat rise from blower)		110 deg F	61.1 deg C	
ambient soil temperature at ~50-75 ft bgs		68 deg F	20.0 deg C	(based on data from North Albuquerque Basin)
target soil temperature		160 deg F	71.1 deg C	
silt/sand thermal conductivity (k)			1.3 * Watts/ m K	* based on average of 1.23 (dry) vs. 1.41 (wet) silt/sand
silt/sand heat capacity			4359 KJ / m3 K	wet soil
silt/sand heat capacity			1906 KJ / m3 K	dry soil
Calculate minimum volume of heated air to heat soil to 160 deg F, and amount of time required to deliver that volume of air				
Determine energy required to heat soil with ___ % moisture content				
Determine energy required to heat the water present in the soil				
moisture content (%)			30	
dry density of soil			1520 kg / m3	
mass of water in 1 m3 of soil at ___ % moisture			651.4 kg	
volume of water in 1 m3 of soil at ___ % moisture			0.651 m3	
$Q = k (T_2 - T_1) / v$ Energy (Q), heat capacity (k), temperature (T), volume (v)				
T1			20 deg C	
T2			71.1 deg C	
water heat capacity			1.3 KJ / m3 K	
Q =			43.3 KJ	
adjust soil heat capacity to account for water content			1949.3 KJ / m3 K	
Determine energy required to heat the soil				
$Q = k (T_2 - T_1) / v$ Energy (Q), heat capacity (k), temperature (T), volume (v)				
T1			20 deg C	
T2			71.1 deg C	
soil heat capacity			1949 KJ / m3 K	
energy to heat 1 m3 of soil from T1 to T2 =			99608 KJ / m3	
cylindrical volume of soil with a height of ___ ft, and a radial distance of ___ ft from the injection well				
height (length of screened interval)			10 ft	
radial distance			12 ft	
volume of cylinder			128.09 m3	
energy to heat cylindrical volume of soil			12758844 KJ	
amount of energy in 1 m3 of heated air				
T1			20 deg C	
T2			77 deg C	(assume heat loss of 5 deg C between blower & well screen)
air heat capacity			1.3 KJ / m3 K	
maximum available energy in 1 m3 of hot air			74.1 KJ	
minimum volume of hot air required			172184 m3	
air injection rate (per injection well)			100 cfm	
minimum time required			42.2 days	
safety factor			2.0	
estimated time required			84.4 days	

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14. ABSTRACT Many environmental contaminants are amenable to degradation by alkaline hydrolysis. This project explored the use of ammonia gas to raise soil pH in order to stimulate alkaline hydrolysis. When ammonia gas dissolves in water, it forms ammonium ion, which consumes hydrogen ions (H ⁺), thereby increasing pH. This study established that 5% ammonia in air can increase soil pH from 7.5 to 10.3. Batch studies indicate that this pH increase can stimulate alkaline hydrolysis reactions, resulting in the degradation of chlorinated propanes (trichloropropane, dichloropropane) and explosives (2,4,6-trinitrotoluene, nitrobenzene, and RDX). A column study was conducted focusing on evaluating the penetration of ammonia and subsequent pH change. The study showed pH penetration of 20 cm in a 2.5 cm diameter column over 7 days, with a flow of 5% ammonia gas at 1 sccm. Chlorinated propane concentrations were reduced from levels of as high as 2400 ug/kg to as low as non-detect. A small amount of these were captured in the column off gas. The team also explored whether ammonia gas exposure could stimulate metabolic activity of ammonia-oxidizing microorganisms. A 283-day experiment did not result in any measureable increase in ammonia-oxidizing microorganisms, but the team found significant increases in soil nitrogen concentrations.					
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